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THE JOURNAL

OF

THE AMERICAN CERAMIC SOCIETY

Vol. 25 November 1, 1942 No. 15

STRENGTH OF BOTTLES AS AFFECTED BY LIMITATIONS OF MANUFACTURING PROCESSES*

By F. W. Preston

Letter of Transmittal

This paper is part of the proceedings of the Standard Testing Procedure Committee of the Glass Container Association of America. The reasons that caused the Committee to ask for a more or less formal statement of what was known on this subject will be apparent from the paper itself. The members of the Committee, namely, Mr. Bowes, Mr. Flint, Mr. Hiller, Mr. Lyon, and Mr. Roche, as well as Mr. Hendrickson, Mr. Lester, myself, and various others associated with the Committee, have read the paper and offered criticisms. Although we do not necessarily, either as individuals or as a Committee, concur in all that is said, we believe that the paper offers a new approach to some difficult problems connected with strength, a primary concern of the Committee, and that it may act as a basis for industrial advances or for further contributions by others outside the Committee.

V. L. Hall, *Secretary*, Glass Container Association

I. Introduction

Bottles are nowadays made by machinery according to a plan laid down years ago by Arbogast,[1] who explained that it must be a two-stage process, involving first the preparation of a blank and then blowing to size in a second set of molds. In hand operation, the glass is "gathered," "marvered," and blown to size without the use of a blank mold.

When the glass is forced against the mold, the skin sets quickly by chilling. The inside parts do not set because they are in contact merely with a tiny mass of air which heats up readily and has little cooling effect. The skin that has set acts as an insulation for the hot glass inside it, and it is only very slowly that the interior can lose heat through the skin.

* Presented by title at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Glass Division). Received April 4, 1942.

[1] Philip Arbogast, of Pittsburgh, Pa., U. S. Pat. 260,879, July 11, 1882; Arbogast's method is essentially the modern press-and-blow operation, pressing the blank solidly in a blank mold, transferring it quickly by means of a two-piece neck mold (ring mold) to a blow mold, and blowing to size and shape. The significance and importance of each fundamental element of apparatus and of timing is fully realized by Arbogast, and what was true then is still true today. There is only one claim at the end of the patent, which is "pressing the mouth or neck to finished form with a dependent mass of glass, withdrawing the plunger, removing the article from the press mold, inserting it in a separate mold, and blowing to form the body."

II. Limitations on Thickness

Whatever the size of the bottle to be made, the temperatures involved are much the same and therefore there tends to be established a set skin of substantially the same thickness. It is fairly easy to chill this skin to a depth of $^1/_{16}$ to $^1/_{18}$ in., but it is not at all easy to make it appreciably thicker. Thus in all sorts and sizes of bottles there is a tendency for some parts, usually the upper parts, to be in round figures about $^1/_{10}$ in. thick. The excess glass tends to go in a mass toward the bottom. Some measure of success has been achieved in spreading it over a large part of the bottle but not over all of it. This is true whatever the manufacturing method, whether gob-fed or suction, and whatever the blowing machine. For instance in that type of bottle known as the "Boston round" (Fig. 1 (*A*)), which is used in a great variety of sizes, the data in Table I were obtained by actual measurement of a number of commercial examples.

Lightweight ware may be considered ware in which the minimum thickness is systematically less than about $^1/_{10}$ in. It can usually be made much more uniform in wall thickness than heavier ware, and it can be made faster, the daily grossage going up rapidly with the easily set walls. It lends itself to special methods of fabrication, as in electric lamp bulbs, which do not use a blank mold.

In the heavier, or normal weight ware, an effort is made to get a maximum wall thickness. This effort

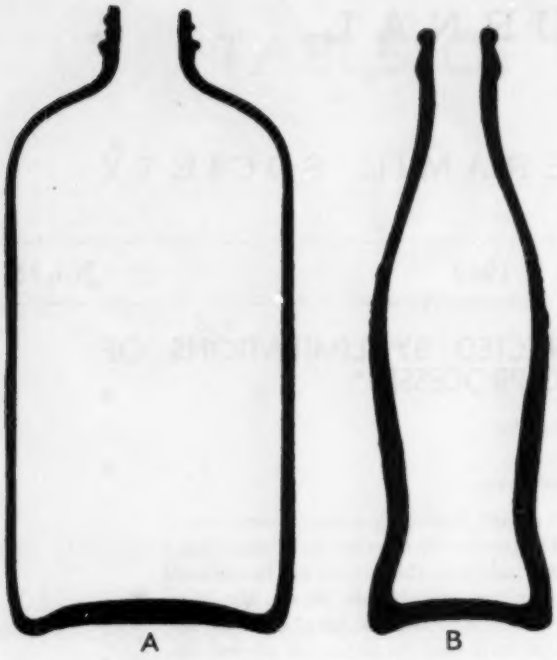

FIG. 1.—Contact prints of bottles; (*A*) Boston round bottles; (*B*) Coca Cola bottles.

rarely achieves anything better than $^1/_8$ in. at the thinnest place. Thus the Coca-Cola bottle, one of the oldest designs, is commonly regarded as the strongest bottle made, and yet it is little thicker than the rest in the upper parts of the neck (Fig. 1 (*B*)), which has an important bearing on its resistance to abuse in the neck area.

III. Effect of Thickness Limitations on Strength

This limitation, imposed by the laws of heat flow, prevents the making of large bottles as "photographed-up" replicas of smaller bottles. Quarts are not oversized pints. It follows that in general the hydrostatic pressure strength of large bottles tends to be less than that of small ones, other conditions being kept as constant as possible. Representative data are given in Table II.

IV. Other Limitations on Bottle Manufacture

It should be pointed out further, however, that capping requirements often call for the same size of finish whatever the size of the bottle. Thus, all soft drinks and sodas, beers, etc., use a standard size of "crown," and all milk bottles (until recently) have used the same size of paper lid.

The inability to distribute the glass uniformly over the mold walls makes it useless to increase the weight of glass in proportion to the size of the bottle; the excess glass goes where it does no good. Thus the "weight to capacity ratio" decreases as the size of the bottle goes up.

The laws governing the heat transfer from the hot inner glass through the chilled skin to the iron of the mold, and thence through the iron, are not well known or at least are not published. Thus it is not easy to calculate how fast bottles can be made on a purely theoretical basis. But on the basis of a vast experience, a new bottle rate of production can be estimated very closely, if the same glass is used; and if the glass is changed but its viscosity curve and certain other data are given, the production rate can be prophesied.* The production rate is, of course, partly a matter of engineering, that is, of the machine and mold design, and as these improve continually, the rate of production steadily increases. It has to, of economic necessity, with the continual pressure to shorten men's working hours, even below the economic limit, as long as it is technically feasible.

TABLE I

MEASUREMENT OF COMMERCIAL GLASS SAMPLES

Capacity (fluid oz.)	Approx. avg. of thickness of glass (suction machine)		
	Shoulder (in.)	Lower side wall (in.)	Center of base (in.)
4	0.100	0.140	0.210
16 (pint)	.090	.150	.270
32 (quart)	.090	.150	.290
128 (gallon)	.100	.150	.330
640 (5 gallons)	.100	.210	.500

TABLE II

AVERAGE INTERNAL PRESSURE STRENGTH OF VARIOUS SIZES OF BOTTLES (lb./sq. in.)

Type of ware	$^1/_2$ pint	Pint	Quart	$^1/_8$ gallon
Steinie beers	590	300	220	160
Ginger ales	460	390	290	
Stubby sodas		440		200

V. Interlocking Variables

The following variables are known to be interconnected, in a complex way, in the art of manufacturing bottles by machine:

(1) Strength of individual bottle (*S*)
(2) Weight " " " (*W*)
(3) Capacity " " " (*C*)
(4) Number of bottles that can be made per minute (*N*)

Thus, a given tank, run at a particular temperature, can melt so many tons of glass per day. The tank is run as hot as practicable; if run hotter, the tank would be melted instead of the glass. Permissible temperatures have been rising steadily for twenty years.

Now if we can melt 60 tons of glass per day, we like to "pull" 60 tons per day, that is, to make 60 tons of bottles per day. This is sound economically, for it costs money to keep a tank hot; hence the more glass that is pulled the less will be the cost per bottle. But apart from that, it is sound technically, for once the glass is adequately melted and homogenized, it will not get appreciably better for stewing; in fact it may get worse from solution of the refractories. But even if it does not get worse, it will not get appreciably better, and it is best to use it as soon as it is fit for use. Among other things, its color is then at the best.

* U. E. Bowes, private communication.

Suppose there are three "shops" on the tank, each capable of using 20 tons of glass per day or approximately 28 lb. of glass per minute. Then it may be readily possible to make 28 bottles, each weighing 1 lb. It will not usually be possible, however, to make 56 bottles, each weighing 8 oz., for speeding up the machines to the extent of making 56 bottles per minute, the inertia forces become troublesome with most types of machine. Apart from the prospect of tearing the machines to pieces, the inertia forces on the glass "blanks" may produce "heel taps," and other troubles. Admittedly, machines having a uniform motion like the Owens suction machine are less troubled with inertia forces than stop-and-start machines of the gob-fed type; admittedly also, 8-arm machines can make more bottles per minute than 6-arm machines; admittedly also double-cavity molds can produce more than single cavities, but none of these factors affects the fundamental problem. We have only to go one stage further and contemplate the difficulty of making 112 bottles per minute of 4-oz. weight or 224 bottles per minute of 2-oz. weight.

If 56 bottles of 8-oz. weight cannot comfortably be made and the production is dropped to 40 such bottles, the pull on the shop is dropped by some 30%. This causes the glass to stay in the tank nearly 50% too long. This is both expensive and unsound. The only remedy is to try to put bottles weighing more than 1 lb. on one of the other "shops" on the same tank.

Now if we put 2-lb. bottles on another shop, we find that we can make more than 14 per minute and that in general we cannot make a technically superior bottle by holding the production down to 14 per minute. Perhaps we can conveniently make 18 per minute, which is about 30% more; this brings the total pull on the tank back to normal. This is a matter well understood by plant operators and is part of the technique of efficient management, though it is not always easy to schedule things so perfectly. Incidentally, the total number of bottles made on the two shops would be nearly the same as before the two changes are made, that is, the "grossage" is the same; but this is not important.

The concern in this paper is not the technique of running a factory, but the technical causes of this technique, and more especially the technical results thereof, namely, the properties of bottles of modern vintage as affected by the manufacturing processes.

Technically our interest is chiefly in the strength, S, of the bottle as affected by the other three variables previously mentioned, namely, the weight, capacity, and rate of production (W, C, and N). It is first necessary to find out what the relationships are in practice between W, C, and N, because these variables are not entirely independent, due to the limitations of the manufacturing problems discussed above. While W, C, and N are not freely variable over wide ranges as independent factors, they are not rigidly interconnected. They can be varied over limited ranges independently; but this variation affects the fourth variable, namely, strength, S.

The operator's problem is to keep W, C, and N within a manageable range. He then tries to adjust them to get optimum results. Outlandish combinations of W and C, for instance, may make operation impossible; that is a matter of design. What relationships the designer has settled on (as the best) will be considered shortly; but having limited the relationship between W and C, the problem is turned over to the operator to find a rate of production, N, that will work. If he cannot do so, the designer must further restrict the relations of weight and capacity. If the operator does succeed in making a bottle according to the designer's ideas, at a rate of operation that is economically sound, the testing department may still throw the bottle out because the strength, S, is inadequate. That situation actually exists today, and tearful designers and salesmen are weeping on the shoulders of the specifications departments.

VI. Weight to Capacity Ratio (WCR)

A fifth variable or parameter has been introduced in practice and found to be a useful concept. Other things being equal, it is a measure of the massiveness or robustness of the bottle, and it is frequently under scrutiny by designers, operators, and testing departments. We shall denote it simply by the symbol, R, where $R = W/C$, and may refer to it simply as the "ratio."

If large bottles were simply small bottles "photographed up," the ratio, R, would be constant throughout the series. If a pint bottle weighed a pound, a quart bottle would weigh two pounds, and a half-gallon bottle would weigh four pounds.

In practice things do not work out this way. The limitations of the manufacturing technique come into play, and large bottles weigh less, in proportion to their capacity, that is, W is not proportional to C, and R or W/C goes down as C goes up.

What is the relationship that has been found, by much experience and experiments, to hold between R and C?

Figure 2 shows a family of curves for seven sorts of bottles.* C is capacity in fluid ounces. The several

* Data from standard blueprints of Glass Container Association.

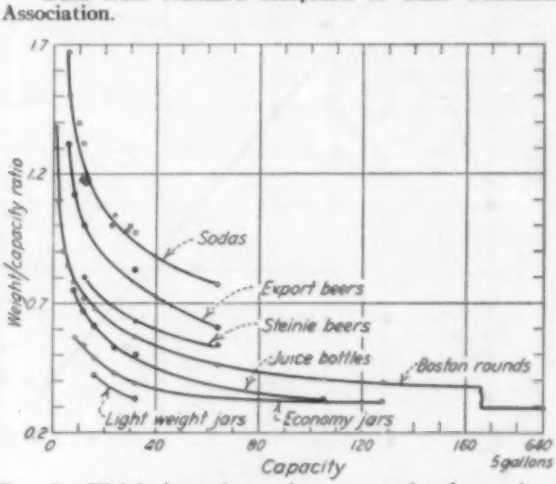

FIG. 2.—Weight/capacity ratio vs. capacity for various classes of bottles and jars.

sorts of bottles differ principally in the matter of shape. Some cover a wide range of sizes, some a very short range. It will be evident that the curves do belong to a family, and the family resemblance is close.

The curves evidently approximate to "generalized rectangular hyperbolas," that is, they have the form $R^m C$ = constant.

If this is the case, then plotting both R and C logarithmically will yield a straight line whose equation is $m \log R + \log C = \log$ (const.).

The most suitable curve to test is the one for "Boston rounds," which is by far the longest and most complete. The 5-gallon capacity point refers to "carboys," which might be regarded as being in the general category of Boston rounds, but cannot be expected to conform exactly to that type. The shape of a Boston round is shown in Fig. 1 (*A*) (a contact print).

The logarithmic plot is given in Fig. 3; and it is clear that a straight line does fit the points very well. The equation of the line is

$$R^4 C = 3.1$$

Where C = capacity in fluid ounces, and $R = W/C$ with W expressed in avoirdupois ounces of glass.

The formula may therefore be converted to read

$$W^4 = 3.1 C^3 \quad W = (1.33) C^{0.75}$$

It should be clearly understood that the index, 0.75, in this formula is not sacrosanct. There is no obvious law of nature to require it. The curve merely represents the accumulated experience of American industry as to how this particular shape of bottle can best be made. Industry knows nothing about any such curve. It merely found by painful experience that particular sizes of this bottle can be best made at particular weights, and it abandoned the attempt to make the bottles much heavier or lighter. Industry thus determined the plotted points which we have now joined up on a curve; and we have found, arbitrarily, a simple equation that fits.

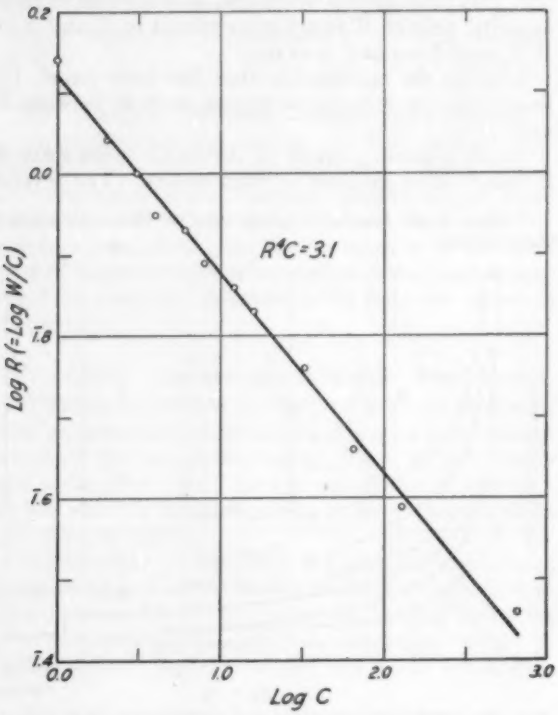

FIG. 3.—Log "ratio" vs. log capacity for Boston rounds.

If the equation of the curve is used to determine what weight a Boston round bottle should have to suit a particular capacity, it will give that weight with considerable precision except at the extreme ends of the curve. At both ends, namely, with extremely small bottles or extremely large ones (carboys), the difficulties of the manufacturer become extreme, and extra glass apparently has to be used. Theoretically, it ought to be possible to make carboys with about 170 oz. of glass. Actually about 190 oz. are used. Evidently $1^1/_2$ lb. of glass are contributed gratuitously, in view of the difficulty of the job, but since it all goes into a slug in the bottom of the bottle, maybe the machine could be improved.

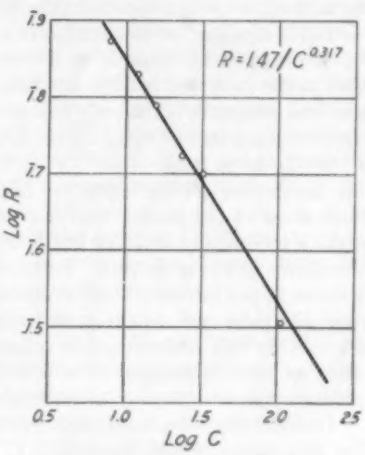

FIG. 4.—Logarithmic plotting for juice bottles.

Referring once more to Fig. 2, the second longest curve is that for fruit-juice bottles. When plotted logarithmically it gives the curve in Fig. 4. This also gives a straight line, but its slope is different. Its equation is approximately

$$R = 1.47/C^{0.32}$$

Combining this information with that from Boston round bottles, it seems likely, in view of Fig. 2, that the appropriate weight, W, for a bottle of given capacity, C, is usually given by some such formula as

$$W = AC^m$$

Where A is a small number, theoretically the weight appropriate for a bottle to hold 1 fluid oz., and m is an index that may vary from about 0.65 to 0.75 with different classes of bottles.

As a check on this, the available data on sodas and steinie beers are plotted logarithmically in Figs. 5 and 6. The sodas are a miscellaneous group, circular in cross section but not necessarily cylindrical. If cylindrical, the proportions are variable, some being much longer and thinner than others, although all are elongated. Thus there is appreciable scatter and some uncertainty as to the relationship between weight and capacity. The curve actually drawn corresponds to

$R = k/C^{0.30}$ which is equivalent to
$W = k_1 C^{0.70}$, where $k = 2.66$

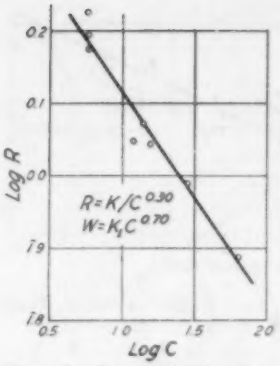

FIG. 5.—Logarithmic plotting for soda bottles.

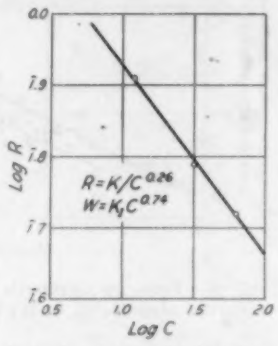

FIG. 6.—Logarithmic plotting for steinie beer bottles.

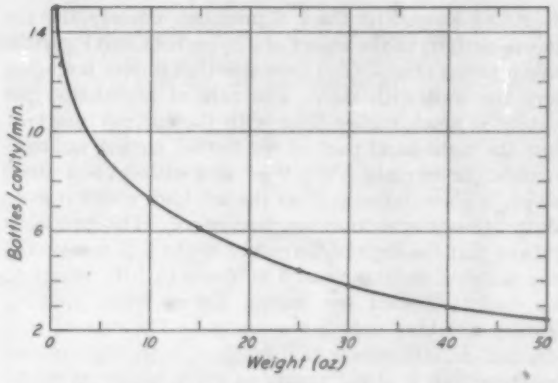

FIG. 7 (*B*).—Production rates for Boston rounds on I. S. machine.

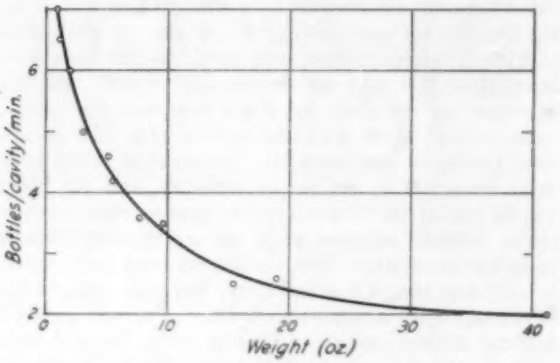

FIG. 7(*A*).—Production rates for Boston rounds on Owens suction machine.

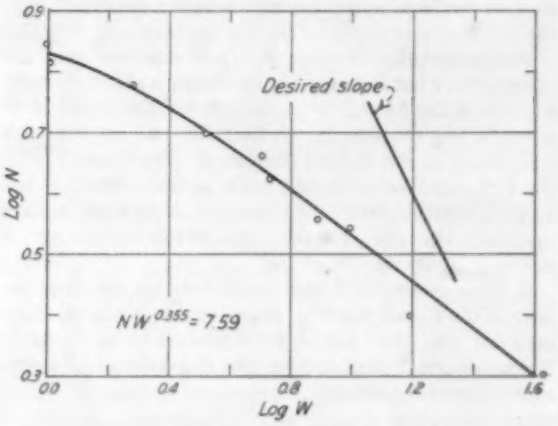

FIG. 7 (*C*).—Logarithmic plotting of production rates for Boston rounds on Owens suction machine.

The steinie beers are less miscellaneous in shape but the points are few. The curve actually drawn corresponds to

$$R = k/C^{0.26} \text{ which is equivalent to}$$
$$W = kC^{0.74}, \text{ where } k = 1.55$$

VII. Rate of Production

With the relationship that seems to be established between weight and capacity, the next question is how weight is connected with rate of production. Figures 7 (*A*) and (*B*) give some information on this point.

Figure 7 (*A*) is actual operating experience in the production of bottles of the Boston-round type on suction machines. The rate of production is expressed in terms of a single "cavity," since multiple cavity molds used on the smaller bottles would otherwise make the result unintelligible.

The curve clearly has the general outlines of a rectangular hyperbola, but a logarithmic plotting of the same data (Fig. 7 (*C*)) indicates that as very small sizes are approached, performance falls off. That is, it falls off below what the trend of the curve in the higher weights would indicate. Over the range of weights from about 2 oz. upward, the curve is a pretty fair (generalized) hyperbola of the form $NW^{0.355} = 7.59$.

Figure 7 (*B*) shows the performance claimed by

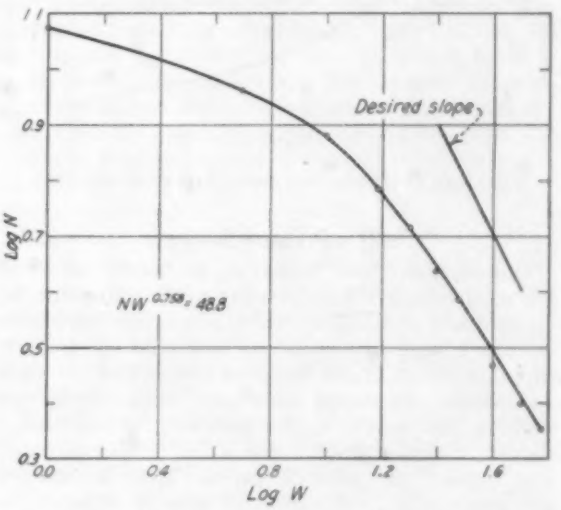

FIG. 7 (*D*).—Logarithmic plotting of production rates on I. S. machine.

Hartford-Empire for the I. S. machine. Clearly, this too has something of the aspect of a hyperbola, but logarithmic plotting (Fig. 7 (*D*)) indicates that it does not agree any too well with this. The rate of production per cavity is much higher than with the suction machine but the right-hand part of the curve, having approximately the formula $NW^{0.748} = 48.8$ with a good steep slope, is quite different from the left half, which is even flatter than the suction-machine curve. This probably means that the high performance of the I. S. machine in the range of weights from 5 lb. down to 1 lb. begins to be badly affected by inertia forces when making bottles weighing only a few ounces. The rate of production is still much higher than with the suction machine, but it is not nearly so much higher as might be expected from the spectacular performance in the higher brackets.

At approximately 100 oz. weight, the suction and I. S. curves would cross, and from this point on, the suction machine would become a better producer than the I. S.

Fundamentally, neither the one machine nor the other gives what is wanted in operating a plant, namely, a curve of the form NW = constant. The index of W is much less than unity, so that the pull on the tank goes down as the weight decreases. The remedy with the I. S. machine is to add more sections, which is not an ideal solution for a quick change; and for the suction machine, the only remedy at present is the use of multiple cavity molds.

A fairly extensive collection of data on the performance of the Lynch machine shows that it is intermediate between the two machines discussed (Fig. 7 (*E*)). There is good deal of scatter, but the order of W seems to be approximately 0.5.

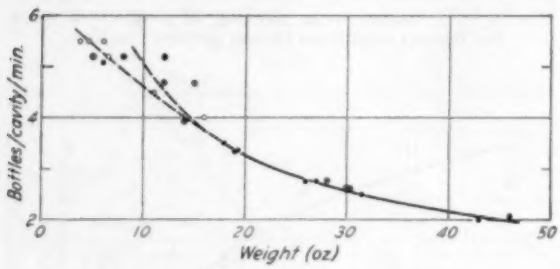

FIG. 7 (*E*).—Production rates on Lynch machine.

VIII. Pressure Strength

Unfortunately, the Boston round bottles on which the most complete data, relating to the connection between weight and capacity, have been secured are bottles on which very little data are available on strength. Strength is best known for those bottles that are made to contain carbonated beverages; such bottles are divisible into subclasses, for instance, "steinie beers," "sodas," "ginger ales," "club sodas," "champagnes," and "siphon" or "seltzer" bottles. Most of these are not made in a great variety of sizes or of weight to capacity ratios. The two most useful categories are the steinie beers and the sodas.

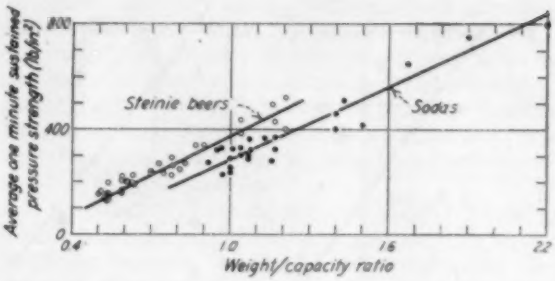

FIG. 8.—Pressure strength vs. weight/capacity ratio (curves abandoned in favor of logarithmic plotting).

Figure 8 shows the scatter plots for these two, from data collected over several years. To a first approximation, the relationship between S and R (strength and ratio)* may be represented by a straight line, but, if so, the lines do not pass through the origin. According to this linear interpretation, soda bottles would have zero strength at $R = 0.35$ and steinies at $R = 0.25$. Bottles of course are not made anywhere near such low ratios; sodas stop at about 0.75 and beers at 0.5. We do not have bottles of zero strength. Our weakest sodas have more than 200 lb. per sq. in. strength, and our beers 125 lb. per sq. in. Therefore, we have no idea how the curve actually behaves near the origin, and there is room for theorizing. From what has been said earlier, it is evident that if bottles of very low ratio were made, they could only be made successfully in very large sizes, holding several gallons of beer or soda. But if such large bottles were made, it is certain they would have some strength, not a zero or negative strength. Thus the straight lines of Fig. 8 cannot be theoretically correct; the line must be curved near the origin, and the theoretical form of the curve must be that of the "generalized parabola,"

$$S = B \cdot R^q$$

Where B and q are constants, and q is not very different from unity.

Plotted logarithmically, this will become

$$\text{Log } S = \log B + q \log R$$

Figure 9 shows the logarithmic scatter plots for sodas.

Figure 10 shows the logarithmic scatter plot for steinie beers. The formulas come out approximately as follows:

$$\text{For sodas, } S = 280\ R^{1/3}$$
$$\text{For beers, } S = 365\ R^{1/3}$$

This means that for a given weight to capacity ratio, the steinie beers are much stronger than sodas. In other words, sodas are somewhat inefficient bottles. An immense amount of glass is used in proportion to the results obtained. Possibly the soda shape should be abandoned, and soda should be bottled in steinie beer shapes, using, however, a more robust variety (higher

* Average 1-minute sustained pressure strength; Hydrostatic Pressure Test on Glass Containers, A.S.T.M. designation C147–40T. American Society for Testing Materials, 260 South Broad St., Philadelphia, Pa.

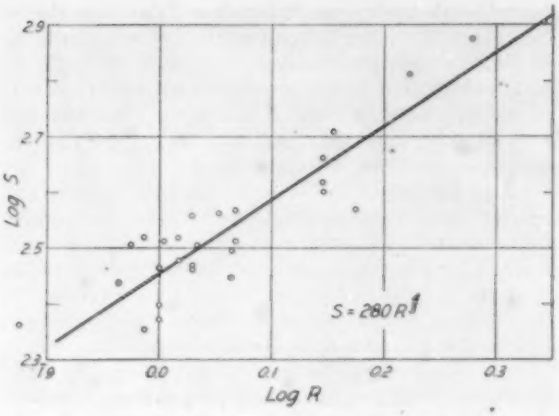

FIG. 9.—Logarithmic scatter plot for soda bottles.

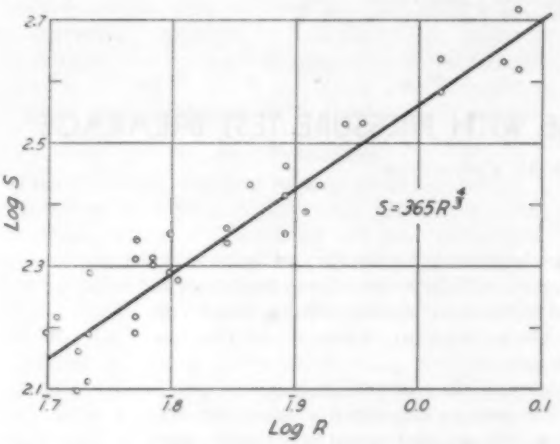

FIG. 10.—Logarithmic scatter plot for steinie beers.

value of R). But this may involve the problem of abuse which is discussed elsewhere.[2]

In Fig. 11 are two curves showing the experimental evidence as to how strength* varies with the size (capacity) of two classes of steinie beer bottles, that is, the one-trip lightweights and the heavier bottles intended for refilling. This plotting, namely, strength and capacity instead of strength and ratio, helps to emphasize the much greater strength of the smaller package.

We now have a set of formulas representing current American experience as to how the quantities W, C, N, and S are interrelated. The relationships are not rigid, but only limited departures seem at present to be practicable.

$W = A_1C^{B_1}$, where B_1 is around 0.[illegible] to 0.75
$N = A_2/W^{B_2}$, where B_2 varies from 0.35 to 0.75 with different machines and different weight ranges
$S = A_3R^{B_3}$, where B_3 is about 1.33

[2] F. W. Preston, "Resistance of Bottles to Abuse," *Glass Ind.*, **23** [6] 217–21, 238 (1942); *Ceram. Abs.*, **21** [8] 168 (1942).

* See star footnote, p. 432.

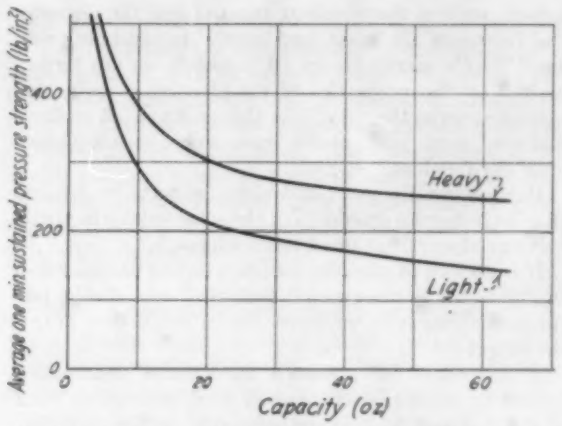

FIG. 11.—Relation of strength to size (capacity) of two classes of steinie beers.

Since the bottle size is always thought of as its capacity, C, these formulas may be better written

$$W = M_1C^{m_1}$$
$$N = M_2/C^{m_2}$$
$$S = M_3/C^{m_3}$$

Where M and m are constants for a particular type of bottle.

At present these tend to come out somewhat as follows:

$$W = M_1C^{0.7}$$
$$N = M_2/C^{0.35}$$
$$S = M_3/C^{0.4}$$

IX. Utility of These Data

This paper has been prepared as a monograph for the Standard Testing Procedure Committee of the Glass Container Association. The strictly scientific technologists will be interested in the relationship between strength and bottle size. The plant operators will be interested in rates of production but will feel that all the mathematics is beside the point. They have found out by experience how fast they can make any particular bottle; they have a few tricks about designing the blanks, and the algebra is "out." There is little to quarrel with in this viewpoint. But the relatively high efficiency designs of some of our modern bottles did not come from the operators or the working designers but primarily from the studies of research organizations of the industry on strength from any angle that seemed to offer any approach.

The users of bottles will not be satisfied either. They will argue that a bottle is nothing but a cover for its contents; that the same beer or soda goes into any bottle, whether large or small, and develops the same pressure there; and that therefore all bottles, of whatever size, should be equally strong and tested at the same level of severity.

It is difficult to reconcile all these attitudes. There is a very limited amount of freedom in the process of making bottles because a number of variables, which might at first sight appear to be independent, as a matter of fact are interrelated in a complex and inconvenient way. We are limited partly by certain laws of

nature, such as those of heat transfer and the viscosity and inertia of the glass, and partly by machine problems, largely inertia forces. Ultimately we are further limited by the properties of the glass as it melts and homogenizes in the tank. As things stand, all of these matters, over and above economic considerations, limit our freedom.

It is useless for users and safety experts to demand that large bottles should have the same safety factor in pressure strength as small bottles have.

It is useless, at present, for operators to demand that machines be so constructed that they can always pull the tank to capacity whatever size of bottle they put on the shops.

It is useless for salesmen to demand that gallon bottles be made as strong as half pints or even, as some of them would like, an unbreakable bottle with zero weight of glass in it.

On the other hand, there is no sense in the purchaser of the bottle, usually the bottler, contending that a substantial bottle has no strength in it and that it ought to be heavier. A modest increase in W, and hence in W/C will produce only that modest increase in strength, S, which is indicated in the graphs shown in this monograph. He should, in general, look to the abuse that he, or the ultimate consumer, may be inflicting on a bottle which is certainly substantial as made.

This paper therefore is written to call attention to the fact that certain factors limit our freedom; to state in outline what these factors are; to urge that interested parties note the limitations and be not unreasonable about them; and to call the attention of inventors to the immense amount of improvement that would be possible if these restrictions could be removed.

The present degree of freedom is presumably indicated by the width of the scatter-plot bands. A widening of these bands would unshackle the industry in noteworthy fashion.

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STUDIES CORRELATING BOTTLING LINE WITH PRESSURE TEST BREAKAGE*

BY A. HERMAN AND H. M. KINDSVATER

ABSTRACT

An investigation was undertaken to determine whether or not the Preston hydrostatic pressure machine, modified so that an initial pressure of 25 lb. per sq. in. may be obtained, is capable of predicting bottling-line production breakage by pressure tests on samples of the bottles in use. The quart and fifth-gallon bottles investigated were round, whereas the pint and half-pint bottles were of the flask type.

Correlating data between production and the percentage of test breakage for quart and pint bottles are significant, and data for fifth gallons, although less significant, are definitely positive. Half-pint data yielded no significant relationship between the percentage of production breakage to test breakage, but this is probably the result of abnormal bottling-line conditions.

A method of determining the range of production breakage percentage to that of test breakage by the use of the standard error of estimate is described.

I. Introduction

Although much work has been done on the physical testing of beverage bottles, no suitable method has been proposed for determining the tensile-strength properties of other classes of bottles, nor has it been proved that any of the standard testing machines will predict directly the ability of a bottle to resist the conditions imposed by high-speed bottling production lines. The purpose of the present experiments, therefore, has been to determine whether or not a significant correlation exists between breakage occurring on the production line and that in a testing machine.

The tests were confined to a single brand of bottles exhibiting characteristic shapes (see Fig. 1). The convex panels of the pints and half pints required that the bottles be run sidewise in certain sections of the conveyer belts in order to feed the star wheels of the different machines by the proper method. Inasmuch as no attempt was made to control the position of the quarts or fifth gallons except during the labeling operation, all bottles were subject to panel and edge impacts.

The Preston hydrostatic pressure machine[1] appeared to be the most useful for testing the strength of bottles because of its universality of application, reproducibility of tests, and availability of the apparatus. The initial pressure exerted by the standard machine is 100 lb. per sq. in., and weights are provided to increase the pressure by stages of 25 or 50 lb. per sq. in. Such a machine obviously would not be acceptable for testing small decanter or flask-type bottles which break under pressures of 25 lb. per sq. in. or less. The weight of the plunger and gear assembly for this reason was decreased to obtain an initial pressure of 25 lb. per sq. in.

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Glass Division). Received April 21, 1942.

[1] (*a*) Hydrostatic Pressure Test on Glass Containers (A.S.T.M. Standard C147–39T), Amer. Soc. for Testing Materials, [Part II] pp. 977–78 (1939); (*b*) revised test C147–40T, *ibid.*, [Part II], pp. 226–28 (1940).

FIG. 1.—Quart, fifth-gallon, pint, and half-pint bottles used in tests.

Suitable weights were provided so that pressures could be successively increased by 5 lb. per sq. in. After the mechanism was started, the operation of the test was entirely automatic until the cycle was completed. Pressure was maintained on the bottle for 60 seconds.

II. Test Procedure

Pressures were adjusted to give approximately 50% of breakage for normal bottles in the preliminary tests. The basis for the 50% breakage test was derived from information published by the American Society for Testing Materials.[1] The Hydrostatic Pressure Test on Glass Containers (A.S.T.M. Standard C147–40T)[1(b)] and also the Thermal Shock Test on Glass Containers (A.S.T.M. Standard C149–40T)[2] state that the prescribed test should be repeated until 50% of the bottles have been broken. Critical pressures (pressures at which 50% of the normal bottles were broken) were established by using a group of bottles representing the various vendors. One portion of these bottles was subjected to a given pressure, and the pressure on another portion was decreased or increased in increments of 5 lb. per sq. in. This procedure was continued until breakages of less than 50% and in excess of the 50% mark were recorded.

The critical pressure was designated as that pressure to the nearest 5 lb. per sq. in. necessary to break 50% of the bottles. From these results, a sustained pressure of 175 lb. per sq. in. for 60 seconds was adopted for the quarts; 200 lb. per sq. in., for fifth gallons; 40 lb. per sq. in., for pints; and 35 lb. per sq. in., for half pints. These pressures were applied to all bottles during the test regardless of vendor.

The serial number of the case of full bottles just produced was recorded first to determine production breakage. Broken bottles were collected, and fractures were analyzed during the test period. The machine in which breakage occurred, the cause of the breakage, if it was known, and the location of the cracks in the bottles were recorded for each broken bottle. Sample bottles were set aside at regular intervals. The experiment was concluded as soon as ninety samples were obtained, the number of cases run was recorded, and from these data, the total number of bottles filled during the test period was computed. The accumulated samples were tested in the pressure machine, and the percentage of breakage was determined. If bottles broken in the testing machine showed poor distribution of glass, this fact was noted. Broken bottles, which had a glass thickness of $^1/_{16}$ in. or less, were designated as those showing poor distribution.

[2] Tentative Method of Thermal Shock Test on Glass Containers (A.S.T.M. Designation C149–40T), Amer. Soc. for Testing Materials, Part II, pp. 232–34 (1940).

III. Conditions Controlled During Testing

The phrase "data obtained under controlled conditions" refers to the steps taken to insure that the form of the curve which is most representative of the observed frequency distribution of the data will usually conform to that outlined by the normal law or by the second approximation equation. This law essentially means that measurements should be taken from day to day under practically identical conditions.

The following sampling procedure was practiced: Bottles were taken directly from the case rather than from the conveyer belt in order to obtain as uniform a sample as possible and also to permit tests to be made on the ware as it was received. One bottle of each mold number in a case was secured. Groups of bottles from additional cases were selected later, but sufficient time intervened between sampling to average one bottle per minute. The total of 90 bottles collected constituted about 1% of those filled during the time that production breakage was being checked.

Inasmuch as the testing machine would show breakage solely as a result of glass failure, only that production breakage arising from this cause was recorded. As an aid in discriminating between glass and machine failure on the production line, the following points were noted: (1) Breakage, in general, occurring in the machines or on the conveyer belts, which could not be attributed to failure of the machine or operator, was designated as glass failure; (2) "machine" or "operator" failure referred, respectively, to breakage arising from poor adjustment and to poor operation of machinery on the line; (3) chipped necks normally occurred as a result of machine failure (this type of failure was also responsible for the breakage of bottles which passed through the capper without receiving caps); and (4) if several bottles were broken successively in a machine, the first breakage was attributed to glass failure, providing such was the cause, and the remainder to machine failure. Breakage of defective or off-specification bottles was not included because this constituted a special type of failure not dependent on tensile strength properties.

The type of machinery (that is, cleaners, fillers, cappers, and labelers) varied from line to line; but because each size of bottle was run on its own line, the effect of the machinery on the data was uniform for each size. The adjustment of the machinery was assumed to be correct from day to day, and treatment resulting therefrom to be consistent. When it was obvious that machinery was poorly adjusted, the resultant breakage was not considered.

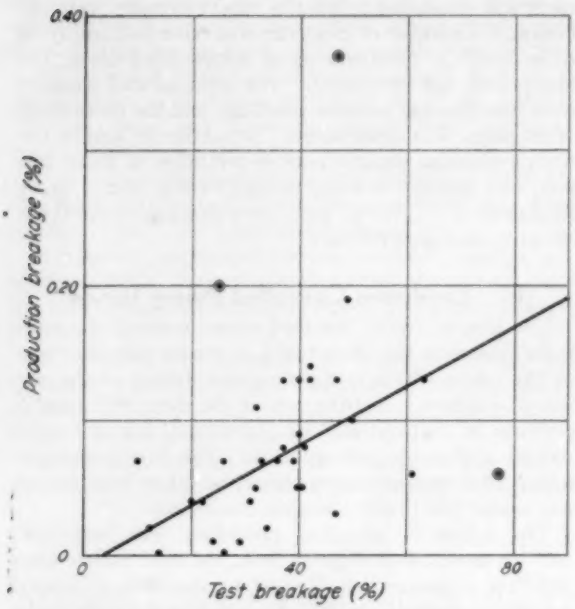

FIG. 2.—Relation between percentage of production and test breakage for quart bottles.

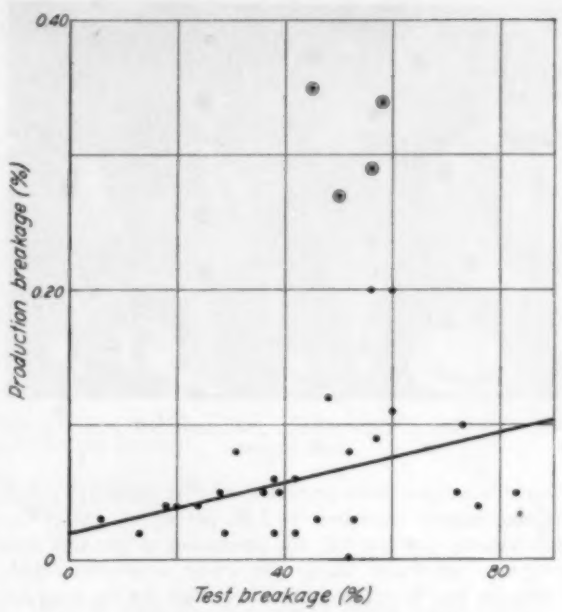

FIG. 3.—Production versus breakage for fifth-gallon bottles.

IV. Experimental Results

The data presented here are based on the performance of 1,460,000 bottles on the bottling lines. The samples, a total of 11,600 bottles, were tested in the pressure machine, using the established critical pressures. An attempt was made to distribute the tests uniformly among the vendors.

Figure 2 shows the relation between the percentage of production and test breakage for quart bottles. Thirty-four individual tests were conducted, and the data of each test are represented by a single point. The line drawn represents the line of best fit for all the points except the three inclosed in circles. The method of calculation of the line of best fit will be discussed later. High production breakage (the upper two encircled points) was the result of bottles which showed poor glass distribution at short and irregular intervals during these tests. In these cases, 92% and 88% of the bottles broken on the production line showed poor distribution, but the small percentage of bottles taken as a sample is not believed to be representative of the bottles under test. High test breakage indicated by the point (production breakage 0.06% and test breakage 77%) was assumed to be the result of the bottles having been weakened for the pressure test by the prominent shear mark. Evidence showing the magnitude of this weakness was supplied by the fact that seven of twelve bottles, taken at regular intervals and concurrently with those for the pressure test, were broken in the standard 75°F. thermal-shock test.

Figure 3 shows the breakage relationship for the fifth-gallon bottles. Thirty-one tests were made, of which four were excluded in the calculation of the line of best fit. The four encircled points showing high production breakage resulted from the same conditions that existed

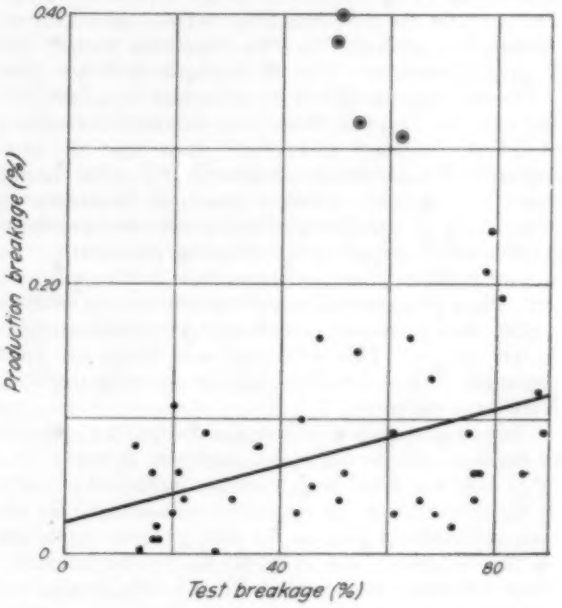

FIG. 4.—Production versus breakage for pint bottles.

for similar quart data. In the order of decreasing percentage of production breakage, 71, 68, 77, and 74%, respectively, of these bottles broken on the production line showed poor glass distribution.

Data on pint bottles are plotted in Fig. 4. Out of the forty-two tests, four were excluded. Points showing 0.31% or more of production breakage in the pint data have been excluded for a different reason. In these cases, the proportion of the bottles broken in the

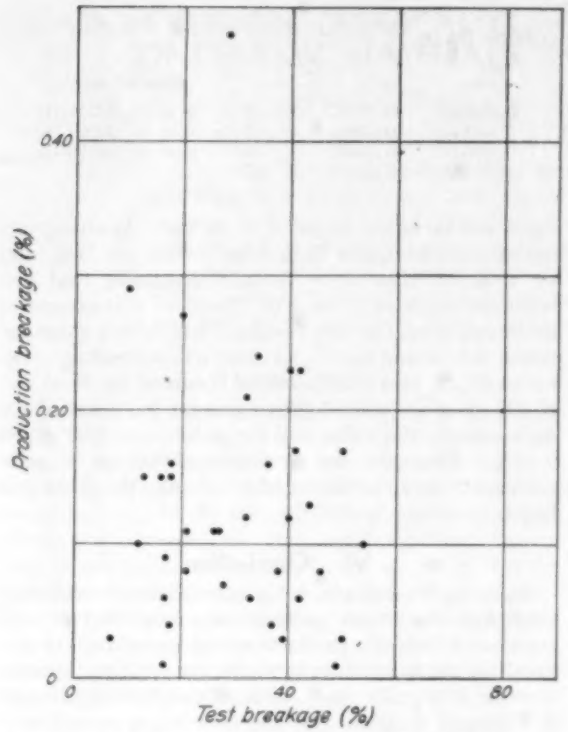

FIG. 5.—Production versus breakage for half pints.

capper alone, in order of decreasing production breakage, was 39, 64, 43, and 48%, respectively. All of these bottles were manufactured by one vendor. During this period of the investigation, bottles sometimes had a high spot on the base at each seam; as a result of the uneven base, the pressure put on the bottle during the capping operation (R. B. capper) may have set up sufficient tension in the bottle to cause failure. Breakage of this type should have been assigned to off-specification or defective bottle breakage, which is not recorded.

Figure 5 represents the data for the half-pint bottles. Thirty-seven sets of data were taken, but they were so erratic that no attempt has been made to calculate the line of best fit. It is believed that the abnormal performance of the half pints may be ascribed to the cleaner on that production line. The adjustment of this cleaner did not remain permanent, and this resulted in the spasmodic bruising of the bottles. This type of cleaner was not used on any other line in the test.

V. Calculation of Correlations

Correlation coefficients for the different sizes have been calculated by the methods of Shewhart.[3] The relations involved in these calculations are defined in Table I, and the results of these calculations are tabulated in Table II. In order to secure accurate values for the coefficients and standard deviations, it was necessary in some cases to carry the calculations as high as eight decimals. The values for the x variables are significant actually to one decimal; for the y variables, to three decimals; and for the correlation coefficient, to three decimals.

In order to test the significance of the correlation coefficients, it is necessary to calculate the probability of such correlations arising by random sampling from an entirely uncorrelated set of observations. If the probability is low, the correlations may be said to be significant. Fisher[4] has published tables derived from his t function, showing the relations between the correlation coefficient, the number of observations, and the probability, P, for the four definite levels of significance, represented by $P = 0.10, 0.05, 0.02$, and 0.01. Moderate observers consider the level P to equal 0.05, or one out of twenty chances, as significant, whereas $P = 0.01$, or one out of one hundred chances is designated as significant by conservative observers. Table III shows the probability of accidental correlations arising from the correlation coefficients which have been obtained, and the coefficients are shown to be sig-

TABLE I

DEFINITIONS OF MATHEMATICAL RELATIONS

X = test breakage (%)
Y = production breakage (%)
n = observations (No.)

Arithmetic mean

$$\bar{X} = \frac{\sum_{i=1}^{n} Xi}{n} \qquad \bar{Y} = \frac{\sum_{i=1}^{n} Yi}{n}$$

Root mean square or standard deviation of the mean

$$\sigma_X = \sqrt{\frac{\sum_{i=1}^{n} (Xi - \bar{X})^2}{n}} = \sqrt{\frac{\sum_{i=1}^{n} Xi^2}{n} - \bar{X}^2}$$

$$\sigma_Y = \sqrt{\frac{\sum_{i=1}^{n} Yi^2}{n} - \bar{Y}^2}$$

Correlation coefficient

$$r_{XY} = \frac{\frac{\sum_{i=1}^{n} XiYi}{n} - \bar{X}\bar{Y}}{\sigma_X \sigma_Y}$$

Standard error of correlation coefficient

$$\sigma_r = \frac{1 - r^2}{\sqrt{n - 1}}$$

Line of best fit minimizing squares of perpendicular deviations of points from line of fit

$$y = -\frac{1}{2r\sigma_X\sigma_Y}\left[(\sigma_X^2 - \sigma_Y^2) - \sqrt{(\sigma_X^2 - \sigma_Y^2)^2 + 4r^2\sigma_X^2\sigma_Y^2}\right] X$$

$$y = Y - \bar{Y}$$
$$x = X - \bar{X}$$

[3] W. A. Shewhart, Economic Control of Quality of Manufactured Product. D. Van Nostrand Co., New York, 1931. xiv + 501 pp.; *Ceram. Abs.*, **11** [12] 870 (1931).

[4] R. A. Fisher, Statistical Methods for Research Workers, 3d ed. Oliver and Boyd, Edinburg, Scotland, 1930.

TABLE II

STATISTICAL SUMMARY OF DATA

Size	No. of Tests	$\bar{X}$	$\bar{Y}$	$\pm\sigma_X$	$\pm\sigma_Y$	r_{XY}	$\pm\sigma_r$	Line of best fit
Quarts	31	35.3448	0.07129	12.4059	0.04682	0.5724	0.12	$y = (0.002160)x$
Fifth gallons	27	44.1481	.06222	19.3404	.04841	0.3668	.17	$y = (0.0009174)x$
Pints	38	50.0000	.07579	24.9241	.05816	0.4497	.13	$y = (0.001049)x$
Half pints	37	30.0541	.12784	12.7766	.09268	−0.0771	.17	

TABLE III

PROBABILITY OF ACCIDENTAL CORRELATION

Size	No. of observations	Correlation coefficient	Probability
Quarts	31	0.5724	<0.01
Fifth gallons	27	.3668	0.061
Pints	38	.4497	<0.01

nificant for quart and pint data and somewhat significant but definitely positive for fifth-gallon data.

Coefficients may vary between ±1, but the correlation is highest when the coefficients approach either of these limits. A correlation of one means that the data may be expressed as a function between y and x as given by the line of best fit and that all points will fall on this line. As the scatter of the points increases, the coefficient naturally decreases.

Another method of evaluating the actual significance of a given coefficient is shown by using the coefficient of alienation or the standard error of estimate. This quantity is defined as

$$s_Y = \sigma_Y\sqrt{1 - r^2}$$

It may be used in the following manner: It is assumed that a sample of bottles gives a certain test breakage and that it is desired to know what production breakage may be expected. From the equation for the line of best fit, it is possible to calculate a value Y_1 from X_1. Then, assuming the conditions to be controlled so that the normal law applies, 68.27 out of 100 groups of identical bottles showing a test breakage of X_1 will have a value for production breakage of $Y_1 \pm s_Y$; for 95.45 out of 100 such groups, a value of $Y_1 \pm 2s_Y$ will be obtained; and that for 99.73 out of 100 such groups, the value will be in the range of $Y_1 \pm 3s_Y$. Applying this information to quart data, wherein $r_{XY} = 0.57$ and $\sigma_Y = 0.047$, then $s_Y = 0.0385$. Assuming that test breakage is 35.34%, then 68.27 out of 100 groups of bottles showing this test breakage will have a value between 0.03% and 0.11% for production breakage; between 0.01% and 0.15% will be obtained for 95.45 out of 100 groups of such bottles; and for 99.73 out of 100 such groups, the value will range between 0.00% and 0.19%. The value for production breakage actually calculated from the line of best fit, using the given test breakage, would be 0.071%.

VI. Conclusions

Analyses of results from the calculation of correlation coefficients and their probabilities show that (1) the correlation between production and percentage of test breakage for quart data is significant; (2) the correlation for fifth-gallon data, although slightly significant, is definitely positive; (3) the correlation arising from pint data is significant; and (4) half-pint data yield no significant relationship between the two breakage percentages, but this is believed to be the result of abnormal bottling-line conditions.

On the basis of these results, it should be possible by suitable refinements of this fundamental technique to predict production breakage from test breakage with close accuracy.

Acknowledgment

The authors are indebted to E. H. Scofield, Director of the Quality Research Laboratory, for his advice on the statistical analysis of data.

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RELATION BETWEEN CHEMICAL COMPOSITION AND DIELECTRIC PROPERTIES OF CERAMIC MATERIALS WITH LOW DIELECTRIC LOSSES*

By M. D. Rigterink, R. O. Grisdale, and S. O. Morgan

Abstract

A number of steatite ceramics were prepared under carefully controlled conditions, and their dielectric losses and direct-current resistances were measured at elevated temperatures. It was found that variations of the ratio of talc to kaolin within certain limits had little effect on the dielectric properties. These properties, however, were changed to a considerable extent by varying the amounts, proportions, and kinds of alkaline earth oxides added as fluxes. The data indicate also that the conditions in a ceramic favorable to a high specific resistance are not necessarily those favorable to a low dielectric loss.

I. Introduction

There is a large and growing field of use for ceramics in the radio and communications industries for which some of the newer special bodies appear to be well adapted. In these uses, such properties as high dielectric strength, low moisture absorption, and good mechanical strength of course are essential, but these requirements offer no particular difficulty. In the matter of low dielectric loss, which is one of the most important requirements in many of the communications applications, some difficulty has been experienced, and this is increased by the trend toward the use of higher frequencies. For some applications, such as power vacuum tubes, the ceramic must not only have low loss at high frequencies but must have these properties at both high and low temperatures.

Hoch[1] has shown that a satisfactory criterion of the power loss to be expected in a dielectric material is the product of its phase angle and its dielectric constant, usually called the loss factor. The energy dissipated in the dielectric (assuming a uniform dissipation) may be calculated quantitatively by the equation,[2]

$$W = 55.5\,\epsilon' \tan\delta \times f \times V^2 \times 10^{-6} \text{ watts}$$

W = power loss per cc.
ϵ' = dielectric constant of material.
Tan δ = tangent of loss angle of material (for values tan δ < 0.1, quantity is substantially equal to power factor).
f = frequency of applied field in cycles/sec.
V = voltage gradient (kv./mm.)

The total energy dissipated at a given frequency and voltage is proportional to the product of the dielectric constant and tan δ, which are constants of the material. This product ϵ' tan δ is the so-called loss factor for which the symbol ϵ'' is frequently used. It is apparent that at very high radio frequencies and high voltages the energy loss will be large unless the loss factor can be made very low.

Fused quartz is often cited as the ideal dielectric of the inorganic type. It does indeed have a low dielectric loss and a dielectric constant lower than most ceramic bodies; it does not, however, lend itself readily to fabrication into many of the complicated shapes which are desirable for many communications uses. The fact that at temperatures above 500°C. the loss in quartz increases to such an extent that it is no longer a good insulating material is also important and is not usually given any consideration. Some ceramic bodies of the so-called steatite type have been developed, which at room temperature have dielectric losses comparable to those of quartz and which also maintain their low loss characteristics at high temperature. These bodies may be readily fabricated by the usual ceramic processes and have excellent mechanical properties. The data to be discussed show that such bodies can be formed from talc-kaolin* mixtures enriched with alkaline earth oxides, so proportioned that the ultimate compositions of the fired materials lie toward the RO–SiO_2 side of a RO–Al_2O_3–SiO_2 triaxial diagram in which RO represents all of the alkaline earth oxides.

II. Procedure

A California talc of high purity, Edgar plastic kaolin, c.p. magnesium, calcium, strontium, and barium carbonates, c.p. beryllium oxide, and distilled water were the raw materials. The chemical analyses of the talc and kaolin as furnished by the suppliers are given in Table I.

The samples were prepared by a typical dry-press process, although wet milling of the mixtures for 20 hours was used to incorporate thoroughly the additions of alkaline earth oxides and carbonates which tended to agglomerate rather than to mix into the batch. As a special precaution against contamination of the batch with injurious ingredients, this milling was done in rubber-lined jars using synthetic sillimanite pebbles. The sample disks, which were approximately 2⅛ in. in diameter and 0.100 in. thick, were fired to dense bodies in a gas-fired, semimuffle furnace whose temperature was controlled to within ±5°C. A typical firing schedule is shown in Fig. 1. From 6 to 6½ hours were required to reach the maturing temperature, which was

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 23, 1942 (White Wares Division). Received May 5, 1942.

[1] E. T. Hoch, "Power Losses in Insulating Materials," *Bell System Tech. Jour.*, **1** [2] 110–16 (1922).

[2] L. Hartshorn, "A Critical Résumé of Recent Work on Dielectrics," *Jour. Inst. Elec. Engrs. (London)*, **64**, 1152–90 (1926).

* These have been called steatite bodies because of their similarity to the insulators obtained when the mineral steatite is fired to a high temperature. The term, "steatite bodies," is extended to include all of those in which talc is the principal ingredient as contrasted to porcelain types in which clay, feldspar, and silica are the principal constituents.

TABLE I

CHEMICAL ANALYSES OF TALCS AND KAOLINS

	A	*B*	*C*	*D*
SiO_2	63.5	61.1	45.5	47.0
MgO	31.7	31.3		0.20
Al_2O_3			39.5	36.8
Fe_2O_3		1.7		0.80
CaO		Trace		0.15
TiO_2				0.18
Alkalis				0.24
Ignition loss	4.8	4.5	14.0	15.0

A, theoretical analysis for talc; *B*, California talc, Whittaker, Clark, and Daniels, Inc.; *C*, theoretical analysis for kaolin; *D*, Edgar plastic kaolin, Edgar Plastic Kaolin Co.

TABLE II

COMPOSITIONS OF MIXTURES USED TO PREPARE SAMPLES

Body designation	Edgar plastic kaolin	Calif. talc	$MgCO_3$
A	30	70	
B	20	80	
C	10	90	
D	20	80	10
E	26	74	20
F	20	80	20
G	14	86	20
H	20	80	30
I	20	80	50
J	10	Forsterite, 90	

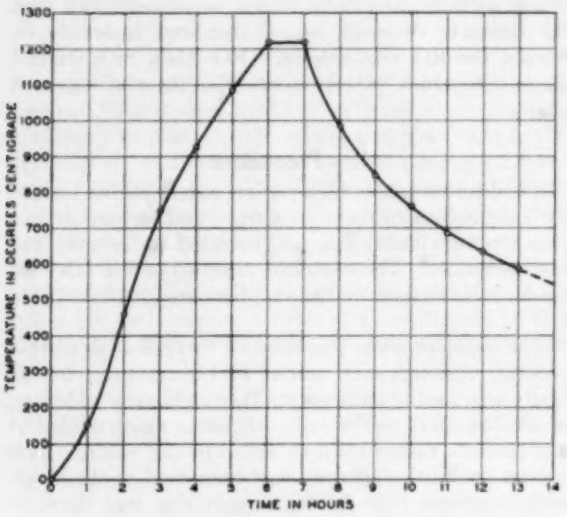


FIG. 1.—Typical firing schedule.

then held for 1 hour. The furnace was turned off completely after this soaking, and the samples were allowed to cool overnight in the furnace.

Silver electrodes were applied to the surfaces of the fired disks by means of burnish silver paste. The values for d.-c. resistance and dielectric loss were measured at several temperatures between 200° and 500°C., and the values for 350° used in the tables and curves were obtained by interpolation. The choice of temperatures higher than those normally used for measurement, and even beyond the limits likely to be reached in most uses of these ceramics, was made because it facilitated distinguishing differences between various materials. The effects of alkali, changes in composition, and structure on the dielectric properties are much more pronounced at 300° to 500°C. than at room temperature. Bodies which show no measurable difference in loss factor at room temperature have been found to be different at high temperature. A body which has low loss at high temperature will invariably have lower loss at room temperature.

The 1-minute d.-c. resistance was measured at 100 volts by the direct-deflection galvanometer method.[3] The values for dielectric loss were determined on a *Q*-meter,[4] which was found to be satisfactory for samples having *Q* values* greater than 10 and could be used without corrections for frequencies from 100 kc. to 3 mc. The measurements of the d.-c. resistance and also of *Q* are probably accurate to ±10%, although variations in temperature may result in the total error being as large as 25%.

III. Bodies of the MgO–Al_2O_3–SiO_2 System

Table II gives the compositions in parts by weight of the mixtures used to prepare the experimental bodies in this system.

The bodies A through J represent a series whose ultimate compositions are shown in Fig. 2 by the points indicated on a portion of the MgO–Al_2O_3–SiO_2 phase equilibrium diagram as published in the collection of Hall and Insley.[5] In calculating these ultimate compositions of the fired samples, the small amounts of impurities are obviously neglected. The results of the *Q* and specific-resistance measurements of these bodies are given in Table III.

Variations in the ratio of talc to kaolin have little influence on the dielectric properties as indicated by the results on the two sets of bodies A, B, and C and E, F, and G; the specific resistance of body C is the only exception to this generalization. There is, however, a considerable variation in *Q*, and specific resistance as the ratio of MgO to Si_2O is increased by the addition of dif-

[3] F. Law, Electrical Measurements, p. 194. McGraw-Hill Book Co., Inc., New York, N. Y., 1938.

[4] Manufactured by Boonton Radio Corp., Boonton, N. J. For a description of the circuit, see H. Thurnauer and A. E. Badger, "Dielectric Loss of Glass at High Frequencies," *Jour. Amer. Ceram. Soc.*, **23** [1] 9–12 (1940).

* The term, *Q*, is used to designate the ratio of reactance to resistance or susceptance to conductance of a coil, condenser, or any circuit element. For the case of an insulating disk, such as was used in this work and which may be represented by loss-free capacitance shunted by a conductance, *G*,

$$Q = \omega C/G = 1/\tan \delta$$

G = equivalent parallel conductance of test sample.
C = its equivalent parallel capacitance.
$\omega = 2\pi \times$ frequency.
The higher the value of *Q*, the less the amount of energy dissipated as heat in a dielectric.

[5] F. P. Hall and H. Insley, "Compilation of Phase-Rule Diagrams of Interest to the Ceramist and Silicate Technologist," *Jour. Amer. Ceram. Soc.*, **16** [10] 459–568 (1933); p. 526.

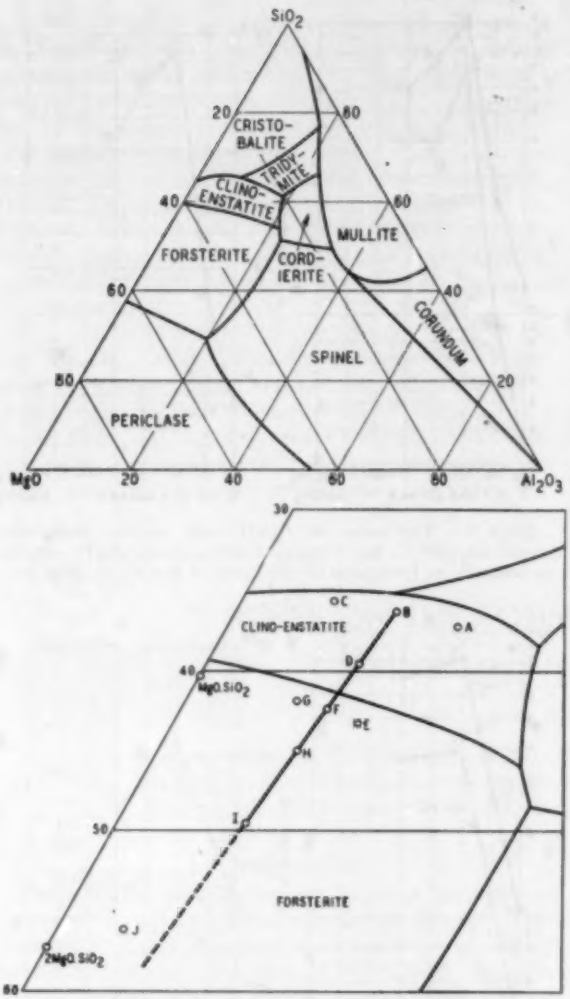


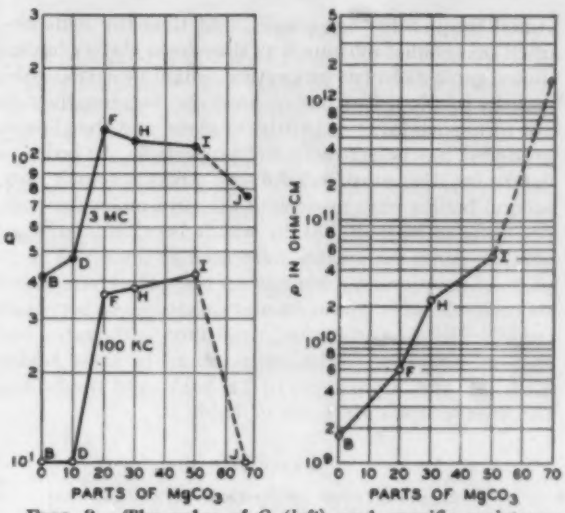
FIG. 2.—Positions of bodies A through J on a $MgO–Al_2O_3–SiO_2$ diagram.

TABLE III

DATA ON SPECIFIC RESISTANCE AND Q OF VARIOUS CERAMIC BODIES

Body designation	Specific resistance at 350°C. (ohm-cm.)	Values of Q at 350°C. 100 kc.	3 mc.
A	1.7×10^9	<10	45
B	1.7×10^9	<10	41
C	1.6×10^{10}	<10	39
D		<10	47
E	7×10^9	25	78
F	6×10^9	36	125
G	7×10^9	28	125
H	2.2×10^{10}	38	115
I	5×10^{10}	42	108
J	1.4×10^{12}	10	77

ferent amounts of magnesium carbonate to a mixture of 20 parts of Edgar plastic kaolin and 80 parts of California talc (bodies B, D, F, H, and I). These results are graphically illustrated in Fig. 3. The addition of 10 parts of magnesium carbonate (body D) caused a small increase in Q, but the addition of 20 parts (body F) caused an increase in Q by a factor of more than three.



FIGS. 3.—The value of Q (*left*) and specific resistance (*right*) at 350°C. as functions of the amount of $MgCO_3$ added to a ceramic body composed of 20 parts of Edgar plastic kaolin and 80 parts of California talc.

With further increase in the MgO content, the Q passes through a maximum and then decreases for a body (J) made from 90 parts of forsterite ($2MgO \cdot SiO_2$) and 10 parts of Edgar plastic kaolin. The forsterite used in preparing this body was made by prefiring the proper mixture of California talc and magnesium carbonate. The composition of body J does not fall on a direct line with the points *B*, *D*, *F*, *H*, and *I* in the $MgO–Al_2O_3–SiO_2$ triaxial diagram. It lies so close to the projected line, however, that the conclusion that Q decreases with further increase in MgO content is probably valid. In contrast to the values of Q, which pass through a maximum, the specific resistance continues to increase as the MgO content is increased. This is an indication that the conditions favorable to a high d.-c. resistance are not necessarily those favorable to a high Q.

IV. Bodies of the $RO–Al_2O_3–SiO_2$ System

In the literature on low-loss ceramics,[6] it has been

[6] (*a*) N. P. Bogoroditskiĭ and I. D. Fridberg, "Dielectric Losses at High Frequencies," *Izvest. Akad. Nauk S.S.S.R.*, **1938**, *Sér. Phys.*, pp. 289–97; *Ceram. Abs.*, **18** [1] 305 (1939).

(*b*) S. Kondo and S. Suzuki, "Physical Properties of Talc and Talc Porcelain by a Particular Method," *Jour. Soc. Chem. Japan*, **40** [Suppl. binding], p. 468 (1937).

(*c*) S. Moriyasu, "Electrical Resistance of Talc–Kaolin System," *Jour. Japan. Ceram. Assn.*, **45** [529] 1–8 (1937); *Ceram. Abs.*, **17** [3] 109 (1938).

(*d*) S. Moriyasu, "Electrical Resistance of Magnesia–Alumina–Silica–Alkali System," *Jour. Japan. Ceram. Assn.*, **45** [530] 77–82 (1937); *Ceram. Abs.*, **17** [3] 108 (1938).

(*e*) S. Moriyasu, "Comparison of Glass and Crystal with Respect to Resistivity," *Jour. Japan. Ceram. Assn.*, **45**, 149 (1937); *Ceram. Abs.*, **16** [11] 343 (1937).

(*f*) Steatit-Magnesia Akt.-Ges., "Ceramic Material," Brit. Pat., 478,794, Feb. 9, 1938 (June 8, 1936); *Ceram. Abs.*, **17** [5] 191 (1938).

(*g*) S. J. McDowell, "Ceramic Body and Method of Making," U. S. Pat., 2,168,230, Aug. 1, 1939 (Sept. 2, 1938); *Ceram. Abs.*, **18** [10] 274 (1939).

stated frequently that alkalis, and thus the feldspars, must be avoided inasmuch as they form glasses having unfavorable dielectric properties. Alkaline earth oxides may be employed as fluxes, however, because they do not form such large quantities of glass, and the glass so produced has better dielectric properties. In order to determine the most satisfactory alkaline earth flux, several bodies were made with the same molecular compositions as body F but in which beryllium oxide or alkaline earth carbonates were used as fluxes. The 20 parts of magnesium carbonate in body F were replaced successively with equimolecular quantities of beryllium oxide, calcium carbonate, strontium carbonate, and barium carbonate. The compositions of these bodies K, L, M, and N are given in Table IV, and the data on the fired samples are given in Table V.

TABLE IV

COMPOSITIONS OF SAMPLE MIXTURES

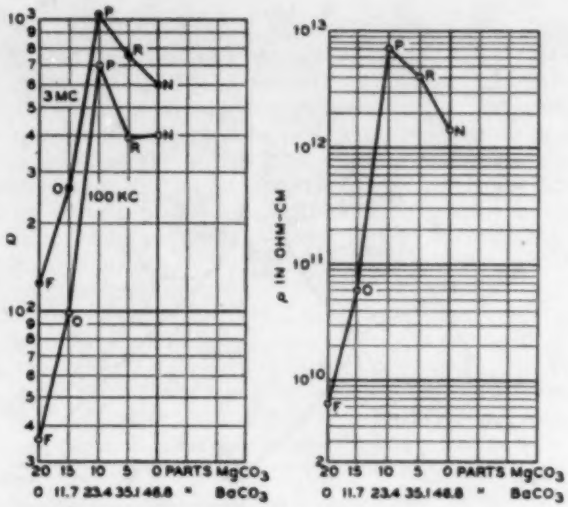
Body designation	Edgar plastic kaolin	Calif. talc	BeO	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
K	20	80	5.93				
L	20	80			23.7		
M	20	80				35.0	
N	20	80					46.8
O	20	80		15			11.7
P	20	80		10			23.4
R	20	80		5			35.1
S	20	80		25			58.5
T	20	80					117.0

TABLE V

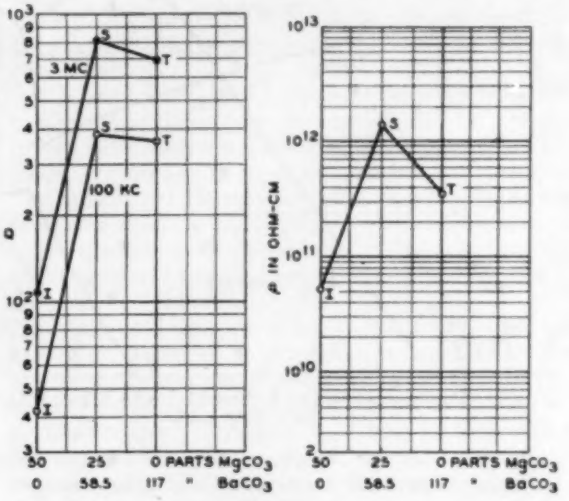
DATA ON SPECIFIC RESISTANCE AND Q OF VARIOUS CERAMIC BODIES

Body designation	Specific resistance at 350°C. (ohm-cm.)	Values of Q at 350°C.	
		100 kc.	3 mc.
K	1.1×10^{12}	13	25
L	4.5×10^{10}	46	230
M	1.8×10^{10}	41	226
N	1.4×10^{12}	400	590
O	6×10^{10}	97	265
P	8×10^{12}	700	1080
R	4×10^{12}	390	750
S	1.4×10^{12}	382	808
T	3.5×10^{11}	355	686

The substitution of beryllium oxide for magnesium carbonate decreased Q, and the substitution of calcium carbonate and strontium carbonate increased Q slightly. The substitution of barium carbonate for magnesium carbonate, however, produced a ceramic with a Q almost five times as large at 3 mc. and more than 10 times as large at 100 kc. The changes in specific resistance are correlated with those for dielectric loss except for body K containing beryllium oxide. The substitution of calcium carbonate and strontium carbonate for magnesium carbonate caused only slight increases in the specific resistance, but the substitution of barium carbonate increased the specific resistance by a factor of more than 100. The substitution of beryllium oxide, however, also improved the specific resistance by a factor of more than 100, offering further evidence that the conditions favorable to a high d.-c. resistance are not necessarily those favorable to a high Q.



FIGS. 4.—The value of Q (*left*) and specific resistance (*right*) at 350°C. for ceramic bodies, molecularly similar to body F, as functions of the ratio of $BaCO_3$ to $MgCO_3$.



FIGS. 5.—The value of Q (*left*) and specific resistance (*right*) at 350°C. for ceramic bodies, molecularly similar to body I, as functions of the ratio of $BaCO_3$ to $MgCO_3$.

V. Bodies of MgO–BaO–Al_2O_3–SiO_2 System

A further study was made of ceramics in which barium carbonate was used as the source of the fluxing oxide. For this purpose, the magnesium carbonate in body F was progressively replaced with equimolecular quantities of barium carbonate. That is to say, first one fourth of the magnesium carbonate, *O*, then one half, *P*, then three fourths, *R*, and finally all, *N*, were replaced with equimolecular quantities of barium carbonate. As shown by the values in Table V and the curves in Fig. 4, both Q and specific resistance pass through maxima which lie at or near the point where one half of the magesium carbonate in the basic body has been replaced with an equimolecular quantity of barium carbonate.

Similar maxima were observed when barium carbonate was progressively substituted for the 50 parts of magnesium carbonate in body I. The maxima in Q and specific resistance illustrated in Fig. 5 occur when half of the magnesium carbonate has been replaced. Not enough values were determined to locate these maxima exactly, and the curves were intended to indicate simply the presence of such maxima. The important observation is that better ceramic products may be produced by the correct combination of two or more alkaline earth oxides as fluxes than by the use of any one by itself.

The results of studies on the effects of methods of preparation, firing schedules, additions of small amounts of alkalis, and the nature and quantities of impurities in the raw materials will be discussed in a future paper. X-ray and microscopic studies are also being pursued in an attempt to furnish a theoretical explanation for the results presented in this paper.

VI. Summary

(1) Variations of the ratio of talc to kaolin within certain limits have little effect on the dielectric properties of low-loss ceramics whose principal constituent is talc.

(2) Large variations in the dielectric properties are caused by variations in the amounts, proportions, and kinds of alkaline earth oxides added as fluxes to a talc-kaolin mixture.

(3) The conditions in a ceramic favorable to high specific resistance are not necessarily those favorable to low dielectric loss.

(4) Differences in dielectric properties of steatite ceramics are more evident in measurements at high temperature than in those at room temperature.

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NOTES ON THE CONSTITUTION OF STEATITE*

By Hans Thurnauer and A. R. Rodriguez

Abstract

A review of the literature is given. A number of steatite bodies, which were given a varying number of firings, were investigated by autoclaving and determining the water absorption in conjunction with microscopic and X-ray methods.

I. Introduction

The term "steatite" refers to a group of ceramic materials which contain hydrous magnesium silicate (talc or soapstone) as a predominant constituent in the unfired condition and which are fired to vitrification. Steatite ceramic materials play an important role as insulators for high-frequency application because of their excellent mechanical properties and low-power losses in the high-frequency field and their high dielectric resistance at room and high temperatures. Because early studies on the constitution of this important industrial material lacked concordance, further work should be done in confirming or extending earlier results.

(1) Review of Literature

From a study of the equilibrium in the oxide systems, Allen, Wright, and Clement[1] found microscopically that there are four magnesium metasilicate forms, namely, (1) clinoenstatite, which is stable at all temperatures; (2) α'-magnesium metasilicate, which corresponds to the natural enstatite or orthorhombic pyroxene; (3) β'-magnesium metasilicate, a monoclinic hornblende, which has no equivalent in nature; and (4) γ'-magnesium metasilicate, a rhombic amphibole which corresponds to kupfferite. The transformation of one modification to another was monotropic according to the authors. The alpha modification was found to form from magnesium metasilicate glass at 1000° to 1100°C. or from melts with sodium feldspar and sodium or potassium silicate; the beta form was obtained by quicker cooling; and the gamma modification, by quenching the silicate melt above the melting temperature. All of the unstable modifications changed to clinoenstatite at 1200°C. or with a flux at a lower temperature.

A fifth modification of magnesium metasilicate was reported by Allen, White, Wright, and Larsen.[2] This was thought to be an enantiotropic modification of clinoenstatite with a transformation point at 1365°C. It was shown later microscopically by Andersen and Bowen[3] to be really forsterite and glass rather than any magnesium metasilicate form.

Bowen and Posnjak,[4] using the X-ray method, showed conclusively that the gamma form, or orthorhombic amphibole, in reality was forsterite and glass and accounted for the observations of Allen, Wright, and Clem-

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Refractories Division). Received April 22, 1942.

[1] E. T. Allen, F. E. Wright, and J. K. Clement, "Minerals of Composition $MgSiO_3$, a Case of Tetramorphism," *Amer. Jour. Sci.*, **22**, 385 (1906).

[2] E. T. Allen, W. P. White, F. E. Wright, and E. S. Larsen, "Diopside and Its Relation to Calcium and Magnesium Metasilicates," *ibid.*, **27**, 15 (1909).

[3] O. Andersen and N. L. Bowen, "The Binary System MgO–SiO_2," *Z. anorg. allgem. Chem.*, **87**, 283 (1914).

[4] N. L. Bowen and E. Posnjak, "Magnesian Amphibole from Dry Melt, a Correction," *Amer. Jour. Sci.*, **22**, 193 (1931).

ent[1] on the basis of the incongruent melting point of magnesium metasilicate and the relation of the indices of refraction of forsterite and magnesium oxide silica glass.

Krause and Leroux[5] investigated the properties of soapstone, from Goepfersgruen, heated at different temperatures. They found that it decomposed at about 900°C. to clinoenstatite and was the only form of magnesium metasilicate observed up to 1400°C. Above 1100°C., cristobalite appeared. Feldspar, according to them, acted as a mineralizer to form clinoenstatite. The crystalline phases were identified by X-ray diffraction.

Haraldsen,[6] likewise using the X-ray method, investigated talc from Norway. It was found that the talc heated to 1000°C. gave a new magnesium metasilicate modification hitherto unknown. Higher heating did not destroy the crystal, but the silica was converted to cristobalite. He was also able to produce it by the reaction of magnesium oxide and silica.

Ewell, Bunting, and Geller[7] studied the thermal decomposition of talc. The molecule of combined water was found to be driven off between 800° and 840°C., accompanied by a large endothermic effect, an increase in true specific gravity from 2.83 to 2.91, and a breakdown of talc into enstatite and amorphous silica. According to these authors, both enstatite and clinoenstatite were present at 1200°C. and only clinoenstatite at 1300°C. At the latter temperature, the amorphous silica was converted to cristobalite as in clays. A further increase of specific gravity from 2.91 to 3.01 occurred on heating talc from 840° to 1435°C.

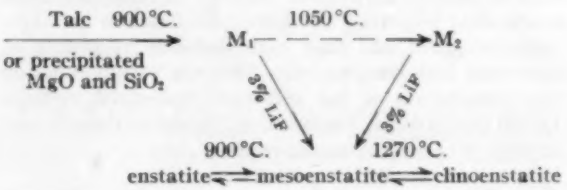
Thilo's[8] X-ray studies on the thermal decomposition of talc verified Haraldsen's results. He called the magnesium metasilicate first formed "metatalk," which he was also able to form from olivine and silica as well as from magnesium oxide and silica at 1250°C. By using 10% of lithium fluoride as mineralizer, "metatalk" was transformed to enstatite at 790°C., and silica was changed to quartz. Efforts to transform enstatite to "metatalk" were unsuccessful; enstatite always converted to clinoenstatite.

Pulfrich[9] made microscopic studies on talc and soapstone heated at different temperatures. At 900°C., he observed the beta modification and glass; at 1200°C., the beta modification, forsterite, and glass; and at 1400°C., the beta modification, enstatite, and glass. He also prepared bodies with 90% of magnesium metasilicate and 10% of kaolin as a basis, fired at 1400°C. With soapstone or talc and kaolin, he found enstatite (beta form) and glass; with periclase, quartz, and kaolin, he found clinoenstatite and glass; and with magnesia, quartz, and kaolin, he found clinoenstatite, enstatite, and glass.

Krause and Jäkel[10] investigated the properties of bodies made of talc, kaolin, and feldspar as relating to the firing temperature, firing time, and firing conditions. Like all ceramic bodies, the strength and the density reached a maximum value by increasing the temperature and firing time. With additional firing, the decrease in strength was attributed to pore formation caused by volatilized alkali.

Büssem, Schusterius, and Stuckardt[11] repeated the work of earlier investigators. Using X-ray diffraction, they confirmed the existence of the magnesium metasilicate form first observed by Haraldsen[6] and later by Thilo,[8] and to which they gave the name "protoenstatite" (Thilo's "metatalk"). The proportion of protoenstatite to clinoenstatite was found to be dependent on the source of the raw materials. The action of several mineralizers, such as lithium oxide, calcium fluoride, boric oxide, and borax, was observed; reaction began at a much lower temperature and the conversion of protoenstatite to clinoenstatite was much faster. Lithium and boric oxides were found to be excellent mineralizers. They accounted for the discrepancies in the earlier investigations to be a result of the transformation of protoenstatite to clinoenstatite caused by pulverization of the material. They also questioned the existence of enstatite as a magnesium metasilicate modification separate from clinoenstatite.

In 1940, Thilo and Rogge[12] observed two new forms of magnesium metasilicate, which they called M_1 and M_2, as well as mesoenstatite (protoenstatite), enstatite, and clinoenstatite. They assert that mesoenstatite, enstatite, and clinoenstatite are stable enantiotropic modifications of magnesium metasilicate, and they give the scheme as follows:



[5] O. Krause and A. Leroux, "Ceramic Magnesium Silicate: II, Vitrification Behavior and Constitution of Ceramic Bodies," *Ber. deut. keram. Ges.*, **10**, 94–104 (1929); *Ceram. Abs.*, **8** [9] 666 (1929).

[6] H. Haraldsen, "Beitrage zur Kenntnis der Thermischen Umbildung des Talks" (Contribution on Status of Thermal Decomposition of Talc), *Neues Jahrb. Mineral. Geog. Beilage*, **61B**, 139 (1930).

[7] R. H. Ewell, E. N. Bunting, and R. F. Geller, "Thermal Decomposition of Talc," *Jour. Research Nat. Bur. Standards*, **15** [5] 551–56 (1935); *Ceram. Abs.*, **15** [2] 76 (1936).

[8] E. Thilo, "Chemical Investigations of Silicates: VII, Magnesium Metasilicate Formed in Thermal Decomposition of Talc," *Ber. deut. chem. Ges.*, **70** [12] 2373–81 (1937); *Ceram. Abs.*, **17** [6] 232 (1938).

[9] M. Pulfrich, "Optical Investigations of Magnesium Silicate Bodies," *Ber. deut. keram. Ges.*, **18** [5] 177–93 (1937); *Ceram. Abs.*, **17** [2] 51 (1938).

[10] O. Krause and E. Jäkel, "Ceramic Firing: VII, Steatite, Data and Methods Used; VIII, Effect of Firing Conditions on Structural Changes; IX, Effect of Firing on Sintering Process; X, Effect of Firing on Properties of Steatite; XI, Summary and Conclusions," *Sprechsaal*, **70** [34] 433–35; [35] 443–47; [36] 455–58; [37] 467–71; [38] 481–82 (1937); *Ceram. Abs.*, **17** [2] 81 (1938).

[11] W. Büssem, C. Schusterius, and K. Stuckardt, "Constitution of Steatite: II, Glass Phase," *Veröffent. Kaiser-Wilhelm Inst. Silikatforsch. Berlin-Dahlem*, **9**, 64 (1938); *Wiss. Veröffent. Siemens-Werken*, **17** [1] 59–77 (1938); *Ceram. Abs.*, **18** [4] 110 (1939).

[12] E. Thilo and G. Rogge, "Chemical Investigation of Silicates: VIII, Thermal Transformation of Anthophyllite, Polymorphism of Mg Metasilicate and Mechanism of Transformation of Anthophyllite and Talc on Heating," *Ber. Deut. Chem. Ges.*, **72B**, 341–62 (1939); *Ceram. Abs.*, **19** [1] 25 (1940).

The earlier studies may be classified into three groups. The first group comprises work on equilibrium in the oxide system, MgO–SiO_2*; the second group deals with the decomposition of the natural mineral talc under heat and resulting reactions†; and the third group discusses technical problems and the determination of the constitution of steatite bodies.‡

Because the constitution of steatite bodies is the subject of the present work, the observations made by Krause and Jäkel[10] and Büssem, Schusterius, and Stuckardt[11] are of special interest. Krause and Jäkel found that the physical properties of steatite bodies change according to firing temperature, time, and conditions, and they attribute the decrease of mechanical strength with further firing to pore formation caused by volatilized alkali. Büssem, Schusterius, and Stuckardt made a similar observation, namely, the decrease of mechanical strength of certain steatite bodies under certain conditions of manufacture. They attribute this decrease to a change in modification of one crystalline phase to another, such as that from protoenstatite into clinoenstatite.

The present writers have made similar observations on certain steatite bodies which had been exposed to prolonged firing or to overfiring, usually indicated by deformation in firing or blistering of the fired object. It could be observed that such overfired pieces had good mechanical strength and high density when leaving the kiln, but their mechanical strength decreased and their porosity increased after a certain period of time. The process of weakening could be accelerated by autoclaving the pieces under steam pressure or by boiling in water for several hours. The purpose of this investigation was to determine the cause of this weakening in structure and to correlate the results with observations of former investigators.

II. Experimental Studies

Various bodies essentially composed of talc and minor ingredients, such as fluxes, were dry milled for 5 hr. in 1-gallon pebble mills and pressed into disks, $1^1/_2$ in. in diameter and $^1/_8$ in. thick. Wedges with an angle of 120 degrees were also pressed, and these were used for taking the X-ray patterns. The pressure applied was approximately 2 tons per sq. in. of area.

The pieces were fired one, two, three, and four times in an oil-fired, production tunnel kiln to a temperature equivalent to cone 14.

The structural changes of the bodies, after each firing cycle, were examined microscopically and by X-ray methods.

Pieces were checked for vitrification after leaving the kiln by immersing them in fuchsine dye-alcohol solution under pressure of 2000 lb. and, after boiling for 4 hr. in water, the moisture absorption was determined. Boiling in water not only served as a means to obtain penetration into existing open pores of the test pieces but was used primarily as a means of accelerating the possible weakening of structure and increase in porosity. The test pieces, regardless of the number of firing cycles, were well vitrified immediately after being taken from the kiln, and they were nonabsorbent. This fact was ascertained by observing the fracture of the dye-tested pieces. No dye penetration was noticeable, even on pieces which later showed high water absorption after boiling in water for 4 hours.

The X-ray diffraction patterns were taken with copper radiation, using a nickel filter, $K = 1.54$ a. u. at 40 kv. and 15 mamp. A circular camera with a radius of 6.12 cm. was used. Exposures were made for 4 hours.

The crystal size representing each sample was estimated roughly by taking the average diameter of an average crystal picked out by inspection from a representative photomicrograph of the sample, magnified 1000 times. Photomicrographs were taken on thin sections of the test specimens.

III. Results

Although a great number of bodies were investigated by the foregoing methods, only four bodies, which are typical of the general behavior of the series of materials investigated, will be discussed.

The four bodies described had the following compositions:

Material	B 1	B 6	B 9	B 15
Calif. talc	89	89	100	70
Feldspar	11			
Flint		3		15
Barium carbonate		8		5
Kaolin				10

Bodies B 1, B 6, and B 15 were well vitrified after each firing cycle immediately after they came out of the kiln as shown by dye-solution penetration tests. Body B9 was porous, because it was made up of pure talc with no flux additions. Figure 9 shows the changes in water absorption with the number of firings after boiling the pieces for four hours.

Bodies B1 and B15 retained their low porosity after four firings, and body B6 exhibited a large increase with repeated firing. The specimens which showed high absorption became chalky after boiling, and the water in which they were boiled separated fine precipitates on cooling, which were identified as magnesium hydroxide and silica gel.

Body B 9 had about the same moisture absorption after the four firing cycles, but the mechanical strength of the test piece fired three times and four times was definitely lower, although no quantitative tests were made.

The growth of the crystals with repeated firing is illustrated in Fig. 5. The microscope was found to be inadequate in identifying the crystal phases so that X-ray diffraction was resorted to.

It was found that the crystal size controlled the absorption and consequent weakening, independent of the heat-treatment, provided sufficient vitrification had taken place. The relationship is shown graphically in Fig. 6. Small crystals favored low absorption and stability with a size of about 7 μ as the limit.

The crystal size was also found to be related to the relative amounts of the magnesium metasilicate modification as detected by X-ray diffraction (Figs. 1, 2, 3, 7, 8, and 9). It will be noticed that bodies B 1 and

* See references 1, 2, 3, and 4.
† See references 5, 6, 7, 8, and 12.
‡ See references 9, 10, and 11.

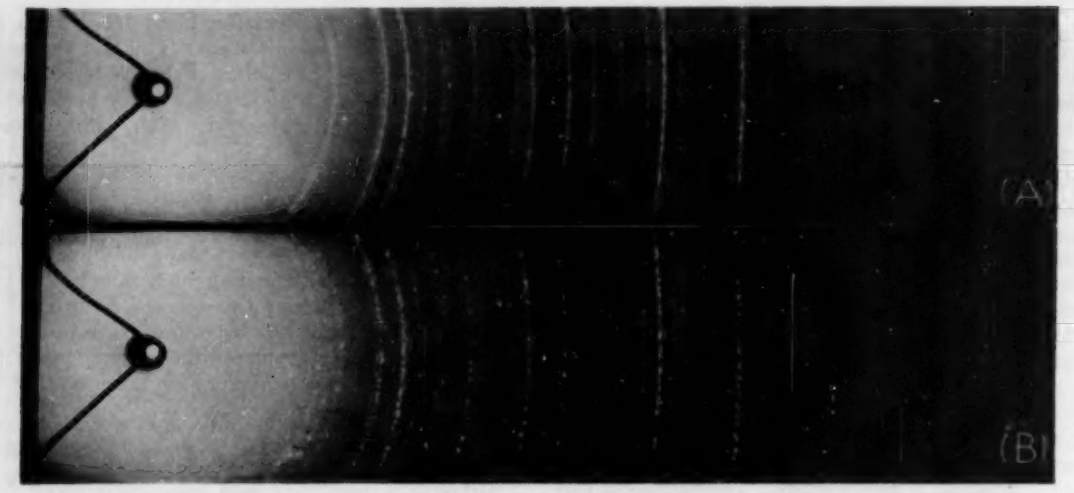


FIG. 1.—X-ray patterns of B 15; (*A*) fired once; (*B*) fired 4 times (little or no transformation).

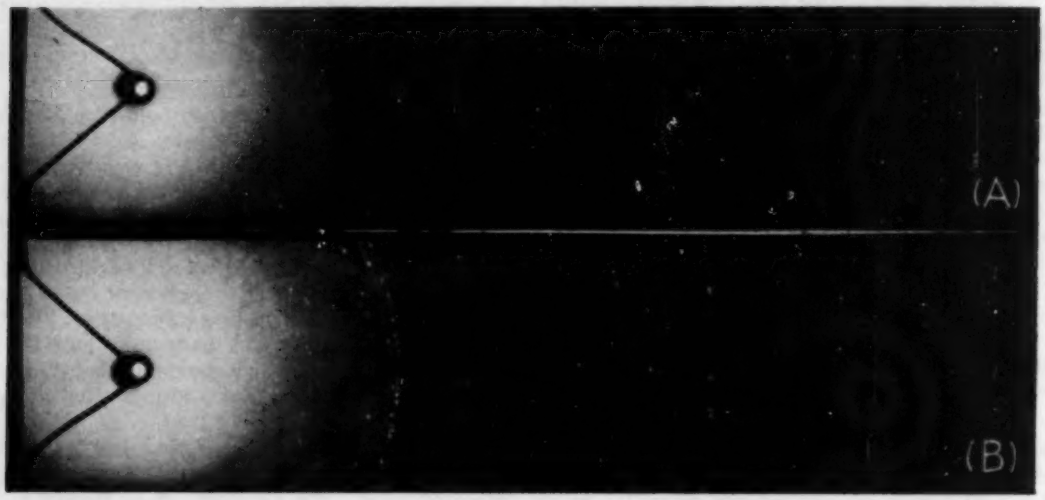


FIG. 2.—X-ray patterns of body B 6; (*A*) fired once; (*B*) fired 4 times (appreciable transformation).

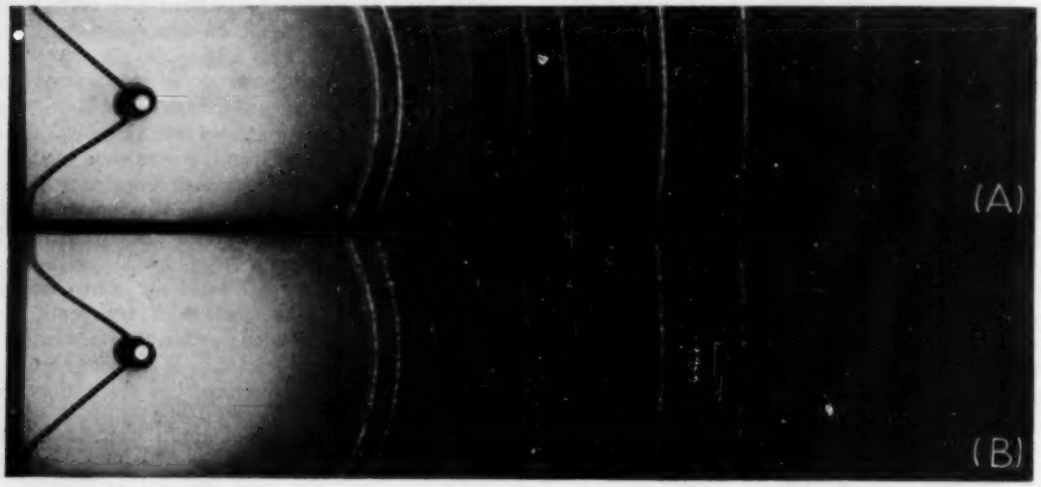


FIG. 3.—X-ray patterns of body B 1; (*A*) fired once; (*B*) fired 4 times (little or no transformation).

B 15 (Figs. 7 and 9) have much smaller crystals than B 6 (Fig. 8). The X-ray patterns of the differently fired specimens of B 1 and B 15 are practically identical (Figs. 1 and 3), indicating that the same crystalline phases were present in about the same proportion after the body was fired once as after it was fired four times. In body B6, however, a new phase predominated after the fourth firing. This is indicated in Fig. 2 (*B*) by the definite weakening of the strong lines of Fig. 2 (*A*) and by the definite strengthening of previously weak lines of Fig. 2 (*A*) in Fig. 2 (*B*), as well as by the appearance of new lines. It shows a transformation of one magnesium metasilicate modification to another.

Powdering the samples in an agate mortar for about $1^1/_2$ hr. brought about a transformation of one magnesium metasilicate form to another, thus confirming the findings of Büssem and Schusterius. This is shown in Fig. 10, in which the original lines have changed completely after powdering the specimen. The relative intensities of adjoining lines of the two modifications also show that more transformation has taken place in the specimen which had the larger crystals, Fig. 9 (*B*).

Cristobalite lines appear in the X-ray samples of all of the samples. Tridymite lines, in addition, appear in B 15, Fig. 1, and in B 6, Fig. 2, and they are faintly present in B 1, Fig. 3.

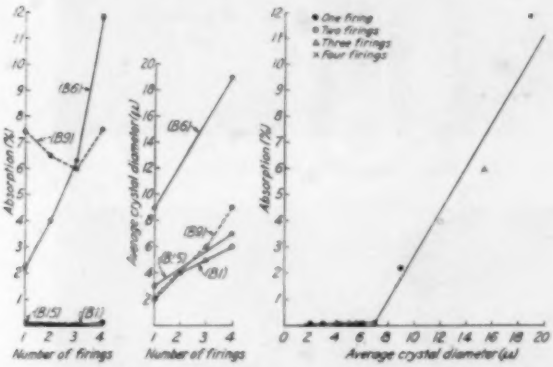


FIG. 4 (*left*).—Heat-treatment and water absorption.
FIG. 5 (*center*).—Heat-treatment and crystal size.
FIG. 6 (*right*).—Crystal size and absorption

IV. Discussion of Results

The large differences in the rates of crystal growth were no doubt the result of the differences in the amount and nature of the glassy phases in the different bodies. The viscosity of the glass definitely would play an important part in conditioning the crystal size, high viscosity favoring small crystals.

Only two crystal modifications of magnesium metasilicate were observed under the conditions of this investigation. One would be called protoenstatite, inasmuch as the X-ray pattern checked closely with the form which Haraldsen discovered and to which Büssem and Schusterius gave that name. This form is unstable. The other was the well-verified stable modification, clinoenstatite.

Protoenstatite must have been formed through a reaction in the solid state because this is the form which first appears when talc decomposes at 850°C. or when pure magnesium oxide and silicon dioxide are heated far below the melting temperature, according to the findings of Haraldsen. Clinoenstatite, however, probably was formed via the liquid phase. In this investigation, protoenstatite was the modification always found in the early stages of the firing or, more specifically, when the crystals remained small, whereas clinoenstatite always appeared when the crystals were large. Powdered talc alone, without the addition of any flux (except for the small amount of impurities it contained), formed mainly protoenstatite with the crystals remaining very small even after ten repeated firings (Fig. 11 (*A* and *B*))

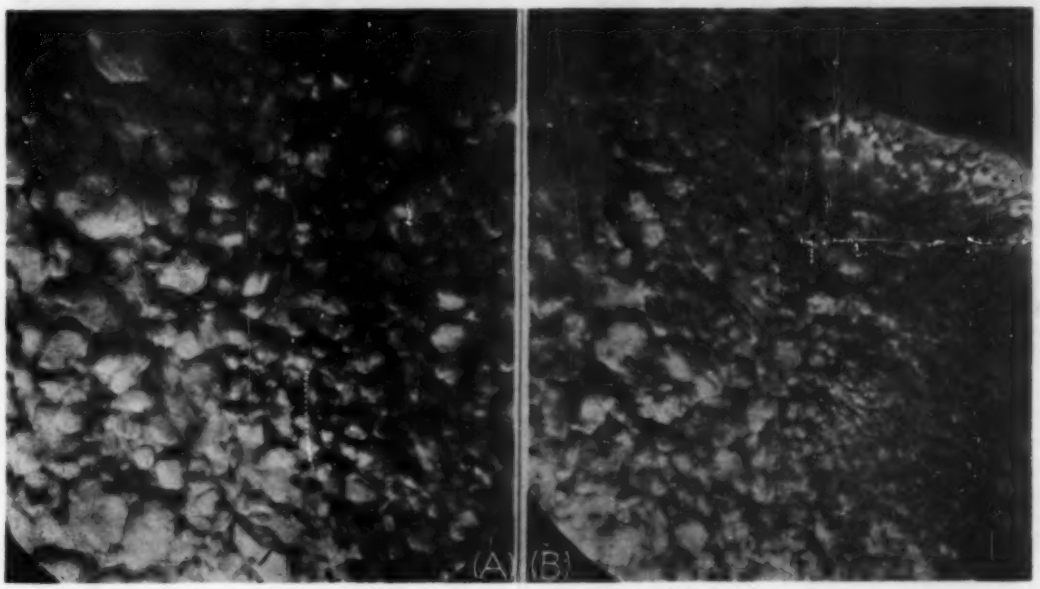


FIG. 7.—Microstructures of body B 1, ×1000; (*A*) fired once; (*B*) fired 4 times.

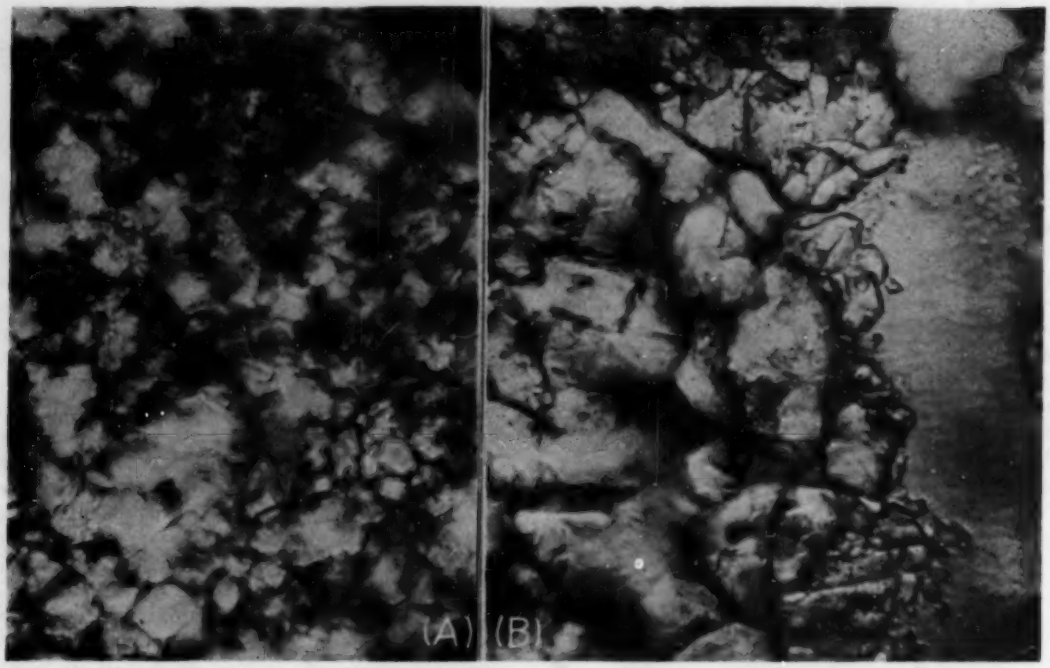


FIG. 8.—Microstructures of body B 6; ×1000; (*A*) fired once; (*B*) fired 4 times.

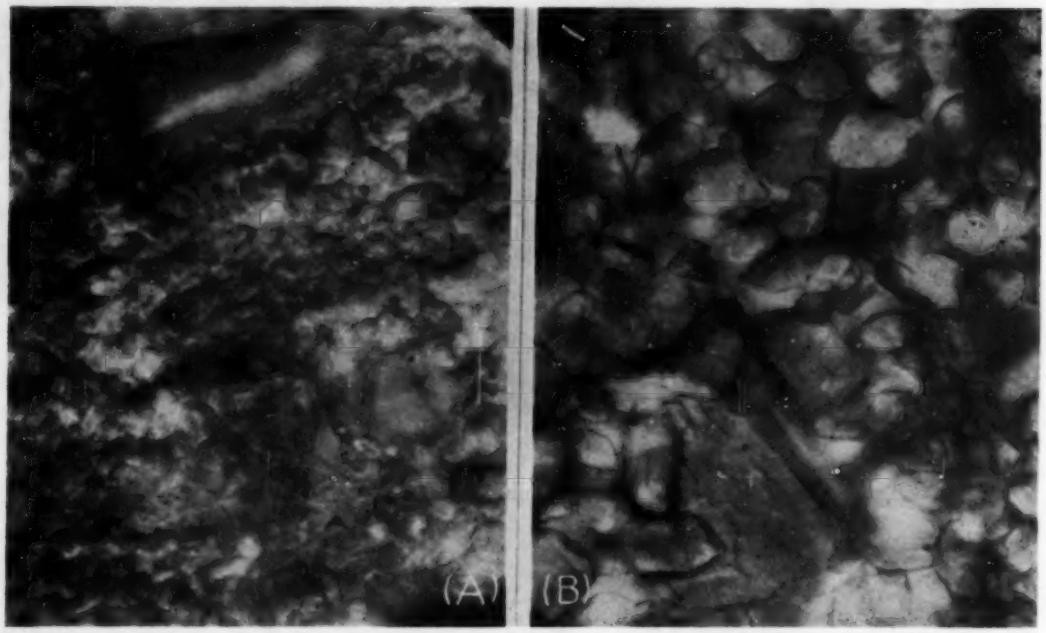


FIG. 9.—Microstructures of body B 15, ×1000; (*A*) fired once; (*B*) fired 4 times.

Evidently, it did not form sufficient melt through which clinoenstatite could crystallize out; for the same reason, the crystals would grow only slowly. When the powdered talc, however, was pressed under high pressure, large crystals and considerable clinoenstatite were formed after four firings (body B 9), Fig. 11 (*C* and *D*). The high pressure must have packed the particles close enough so that the small amount of flux present in the talc as impurities had a better chance to react to form a liquid phase.

This dependence of transformation to crystal size is shown in Figs. 1, 2, 3, 7, 8, and 9. Although these bodies were sufficiently vitrified, the nature of the glass in each differs so that in one the unstable form of magnesium metasilicate was essentially retained and in the other, the stable form made its appearance. In those

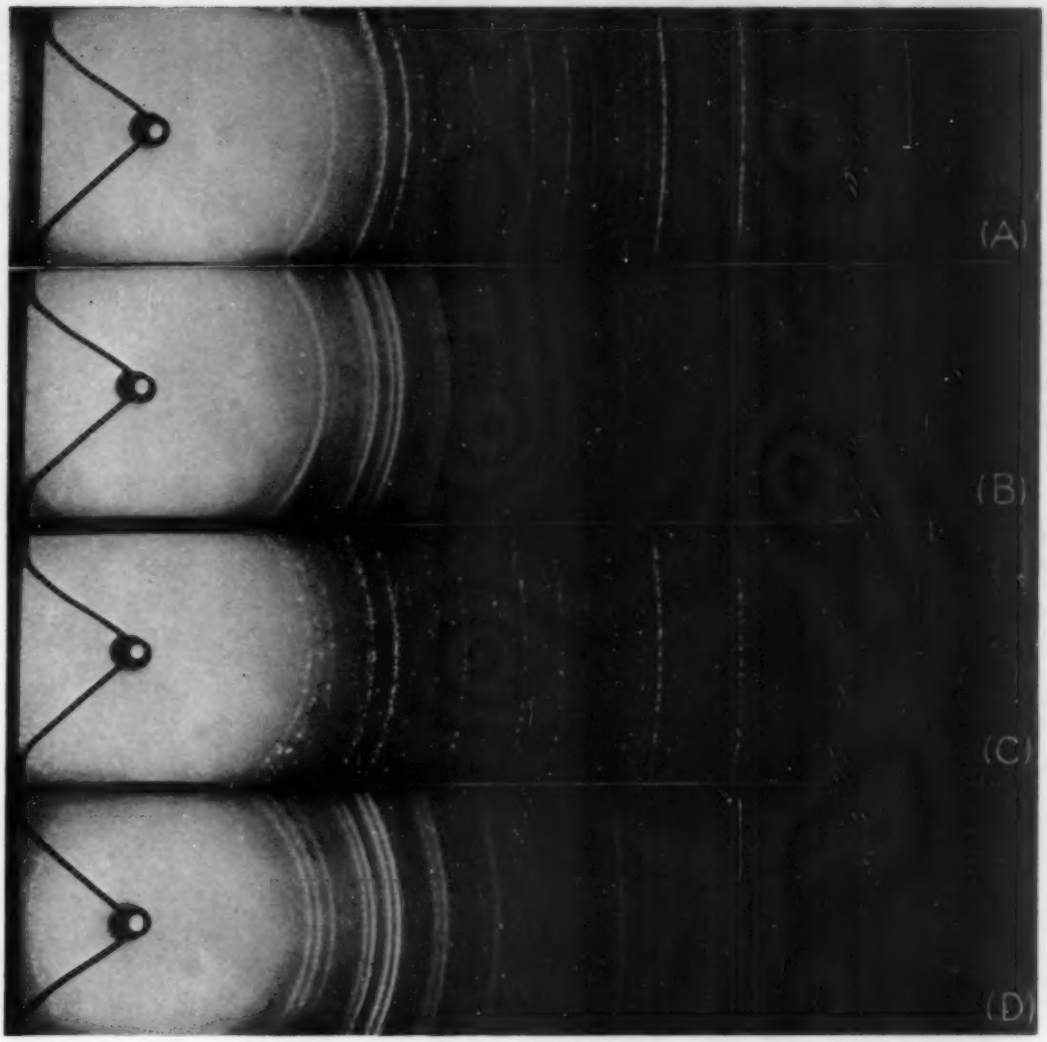


FIG. 10.—X-ray patterns showing transformation of one magnesium metasilicate to another caused by pulverization; body B 15; (*A*) fired once (unpowdered); (*B*) fired once (powdered for 1½ hr.); (*C*) fired 4 times (unpowdered); (*D*) fired 4 times (powdered for 1½ hr.).

specimens in which the protoenstatite form persisted with repeated firings, the glass must have had little action on the crystals.

The transformation brought about by pulverization suggests that the two crystal structures are possibly closely related. One structure could probably go to the other by the mere gliding of planes which is brought about by the shear stress in grinding. The somewhat greater extent of transformation occurring in specimen B15 that was fired four times (Fig. 10 (*D*)) compared to that fired once (Fig. 10 (*B*)) was probably the effect of its larger crystals on which the grinding action would be more effective.

This result at once raises the question as to whether or not the increase in absorption that occurred in the boiling test and after extended heat-treatment may be caused by transformation of protoenstatite to clinoenstatite in accordance with the conclusion reached by Büssem and Schusterius. No difference could be detected, however, in the X-ray patterns of the boiled and unboiled pieces. Büssem and Schusterius do not give data on the crystal sizes of their bodies.

It seems probable that the weakening may be explained on the basis of crystal size alone. The crystal size apparently determines the strength, independent of the heat-treatment in bodies with sufficient vitrification. Provided the crystals are kept small enough (not more than 7 μ) (Fig. 6), the body would remain dense regardless of the number of firings it has received. Large crystals would have a greater tendency to crack than smaller sizes when subjected to strain. These cracks would furnish the channels for the absorption and weakening. The strain may be brought about by temperature changes, or it may be caused by the differences in expansion between the crystalline and glassy phases.

It seems more likely that the weakening of the body is

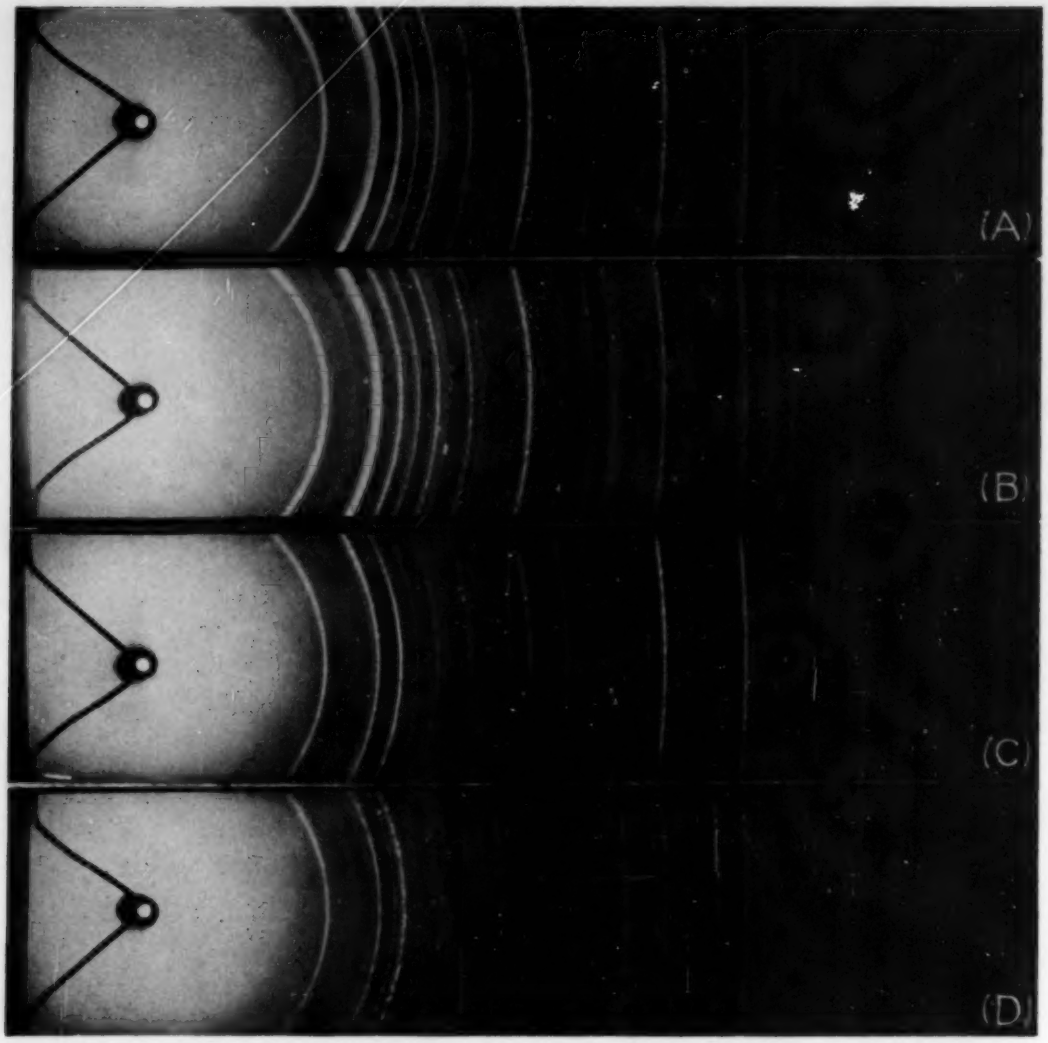


FIG. 11.—X-ray patterns; (*A*) talc calcined 5 times; (*B*) talc calcined 10 times; (*C*) body B 9 fired once; (*D*) body B 9 fired 4 times (note transformation).

caused by the mechanical cracking of large crystals of clinoenstatite and not by transformation as concluded by Büssem and Schusterius.

Acknowledgment

This work was carried out in conjunction with the Department of Ceramic Engineering, University of Illinois, to which the authors are greatly indebted for the use of the equipment. To C. W. Parmelee, head of the department, in particular, the writers are grateful for his kind cooperation and supervision, without which the work could not have been successfully conducted. The writers also take pleasure in thanking the Illinois State Geological Survey and W. F. Bradley, in particular, for the use of the X-ray equipment.

AMERICAN LAVA CORPORATION
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APPARATUS FOR MEASURING THERMAL CONDUCTIVITY OF REFRACTORIES*

By C. L. Norton, Jr.†

Abstract

An apparatus for measuring the thermal conductivity of refractories is described in detail, and results are shown for several types of insulating refractories. Comparisons are made from data which were obtained on a low-temperature plate tester, and the effect of several variables on measured heat flow are discussed.

I. Introduction

For many years, discrepancies have occurred in the thermal conductivity values which have been measured in different laboratories. This condition has been a source of concern to manufacturers of refractories, particularly to those producing insulating firebrick. Because no standard test procedure has been established, several different types of apparatus have been used by producers and consulting laboratories with the result that strictly comparable values have not been available to the consumer. The data presented here have been developed in the Babcock and Wilcox Company laboratory in connection with a cooperative program with the Johns-Manville Company in an attempt to establish a basis for standardization.

(1) Previous Work

Nicholls[1] has described a series of cooperative tests made by different laboratories on samples of fireclay and silica refractories, and Fig. 1 is reproduced from his paper to show diagrams of the forms of apparatus which were in general use in 1936. The type of apparatus used originally in this laboratory and described by Wilkes[2] and later by Austin and Pierce[3] seemed to offer the most advantages. These may be listed as follows: (1) By using silicon carbide heating elements, higher hot-face temperatures may be reached than with the other forms of electrical heating shown in Fig. 1; (2) the use of a water-flow calorimeter allows a direct measurement of heat flow, and it does not depend on a secondary reference which may be subject to change; (3) owing to the low mass of the tester, thermal equilibrium may be established in a relatively short time; and (4) by limiting the power input to the Globar resistance elements, stray electromotive forces that may affect thermocouple readings are reduced to a minimum.

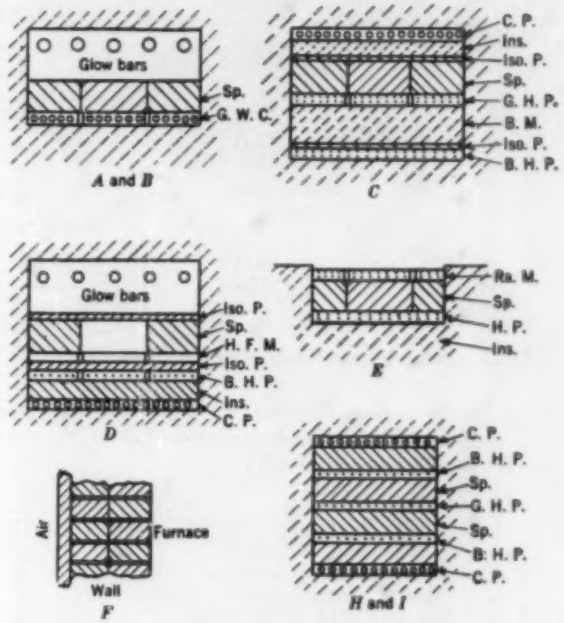

Fig. 1.—Diagrams of apparatus for determining thermal conductivity (after Nicholls[1]).

B.H.P., balancing hot plate — *H.P.*, hot plate
B.M., balancing meter — *H.F.M.*, heat flowmeter
C.P., cold plate — *Iso.P.*, isothermal plate
G.H.P., guarded hot plate — *Ra.M.*, radiation meter
G.W.C., guarded water calorimeter — *Sp.*, specimen

(*A* and *B*): G. B. Wilkes,[2] Mass. Inst. of Technology; J. B. Austin and R. H. H. Pierce, Jr. [3(a)]; (*C*): J. L. Finck, J. L. Finck Lab., *Jour. Amer. Ceram. Soc.*, **18** [1] 6–12 (1935); (*D*): C. E. Weinland,[4] Johns-Manville Lab.; (*E*): C. A. Peterson, Armstrong Cork Co. Central Tech. Lab., *ibid.*, **18** [4] 128–34 (1935); (*F*): R. H. Heilman and R. S. Bradley, A. P. Green Firebrick Co., *ibid.*, **18** [2] 43–48 (1935); (*G*): G. B. Wilkes, description of apparatus in (*A*), *ibid.*, **16** [3] 175–230 (1933); (*H* and *I*): R. H. Heilman, *Trans. Amer. Inst. Chem. Engrs.*, **18**, 283–93 (1926) (abstracted in *Mech. Eng.*, see *Ceram. Abs.*, **6** [2] 65 (1927)); M. L. Hartmann, O. B. Westmont, and C. E. Weinland, *Proc. Amer. Soc. Testing Materials*, **28** [Part II] 820–47 (1928); *Ceram. Abs.*, **8** [8] 341 (1929); (descriptions of guarded hot-plate method with samples on both sides).

To operate the tester, a known thickness of sample is maintained with a temperature difference between the hot and cold faces. The heat flows from the hot to the cold face and passes into the water-cooled copper calorimeter. By measuring the temperature rise of the water passing through the calorimeter and the weight of water flowing for a measured time interval,

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* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 21, 1942 (Refractories Division). Received April 21, 1942.

† Research director, Refractories Division, Babcock & Wilcox Company.

[1] P. Nicholls, "Determination of Thermal Conductivity of Refractories," *Bull. Amer. Ceram. Soc.*, **15** [2] 37–51 (1936); p. 38.

[2] G. B. Wilkes, "Thermal Conductivity of Refractories," *Jour. Amer. Ceram. Soc.*, **17** [6] 173–77 (1934).

[3] (*a*) J. B. Austin and R. H. H. Pierce, Jr., "Reliability of Measurements of Thermal Conductivity of Refractory Brick," *ibid.*, **18** [2] 48–54 (1935).

(*b*) For bibliography on heat-transfer measurements, see references listed by J. B. Austin in "Symposium on Thermal Insulating Materials," pp. 65–67. Amer. Soc. Testing Materials, 1939; *Ceram. Abs.*, **20** [2] 45; [4] 97 (1941).

TABLE I
SAMPLE DATA SHEET*

Time	Specimen thermocouple 1	2	3	Δt	W	W·Δt	Balance $l_g - r_g$	cal − g	In H_2O (°F.)	Room temp. (°F.)
9:30	6.954	22.81	8.82	0.529	373	197	±0	+1.0	69	72
10:30	6.953	22.81	8.83	0.527	374	197	±0	+0.6	70	72
11:30	6.954	22.83	8.85	0.533	373	199	±0	+0.4	70	72
3:00	6.952	22.85	8.83	0.532	373	198	±0	1.4	72	74
Avg.	6.954	22.82	8.83				$Q = 197.7 \times 4.7 = 928$ B.t.u./hr./sq. ft.			
Corr.	+0.031	+0.06	−0.05	2.45°C./mv.						
Corr. avg.	6.985	22.88	8.78							
t or Δt	1415°F.	1027°F.	421°F.	1.3°C.						

Time 11:00 Exit temp. (°C.)	
Cal.	22.3
lg	22.5
rg	22.5
og	24.6

Exit flows (cc./minute)	
lg	860
rg	1000
og	850

1415	1415	1027
−1027	−421	−421
388	994	606
+194	+497	+303
1221	918	724

$$k_{1221} = \frac{928 \times 0.93}{388} = 2.22$$

$$k_{918} = \frac{928 \times 1.95}{994} = 1.82$$

$$k_{724} = \frac{928 \times 1.02}{606} = 1.56$$

Control point, 8.55; amp., on 15.5, off 14.8; volts, on 109, off 114; transtat setting, 101; line voltage, 110.

* Left guard, lg; right guard, rg; outer guard, og.

the quantity of heat absorbed by the calorimeter may be determined. The conductivity coefficient, k_f, may be computed from equation (1).

$$Q = \frac{K_f \times A \times (T_1 - T_2)}{l}. \qquad (1)$$

Q = heat transfer per hr. through area A.
A = area of material conducting heat.
T_1 = hot-face temp. of material.
T_2 = cold-face temp. of material.
l = thickness of material.

Table I shows a sample data sheet.

Several arrangements of apparatus have been used following that described by Wilkes[2] as well as one previously used in this laboratory. A great variation, however, occurs in measured values obtained by these different testers, and the values diverge about as much as those obtained from test apparatus of different basic design.

Figure 2 shows results obtained on one brand of insulating firebrick from five laboratories in which Globar-heated, water-flow calorimeter types of apparatus were used. These results show that to obtain reproducible results from different laboratories the standardization of construction and operation is even more important than the general design.

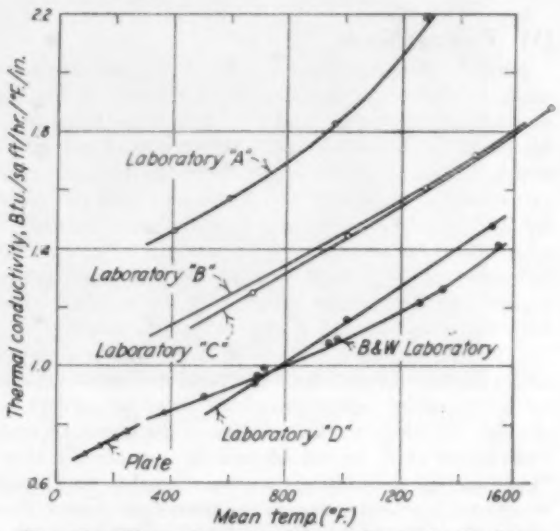


FIG. 2.—Thermal conductivity of sample B determined by five laboratories using Globar-type water calorimeter testers compared with plate-tester values.

II. Description of Apparatus

Figures 3 and 4 show the general appearance of the tester, and Fig. 5 shows a section through the furnace. The construction of the heating systems and also for the water, calorimeter, and thermocouple systems is described.

(1) Heating System

Heat is supplied to the upper furnace section by six air-cooled Globars.* These heating units may be operated to 2800°F. or as low as 400°F. on the hot face of the test sample. The life of the Globars exceeds 3000 hours of operation, but their resistance increases over a period of months. They are connected in series when the bars are new, and combinations of series and parallel connections may be used later when the unit resistance has increased. Figure 6 shows the circuit between the power supply and the heating unit. The power supply should be capable of delivering up to 50 amp. with a controlled variable voltage of between 30 and 230

* Type AT Globars (68 volts, 52 amp., 34–14 length, 3/4 diam.) from Carborundum Co., Globar Division.

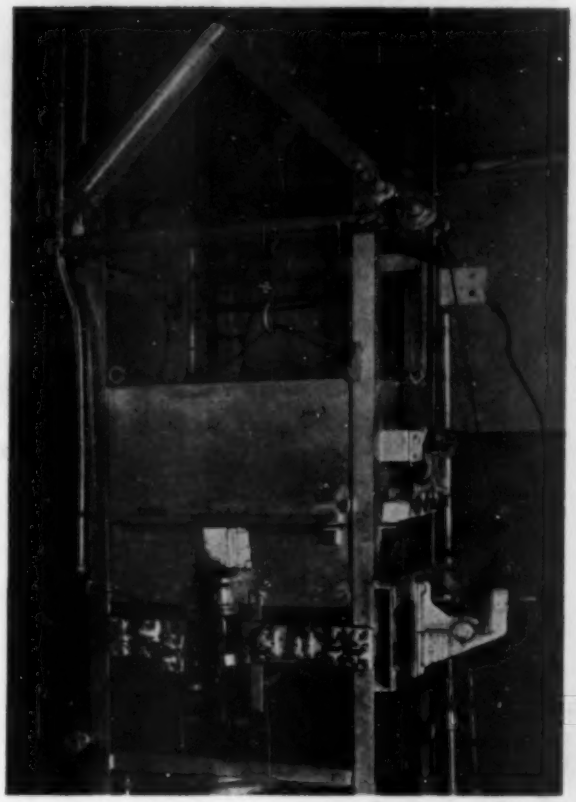


FIG. 3.—Thermal conductivity testing apparatus.

FIG. 4.—Thermal conductivity testing apparatus.

volts. A motor-generator set or an elaborate voltage stabilizer is not required inasmuch as the operation of the by-pass resistance will take care of normal line fluctuations. With a controlling potentiometer and with normal line voltage as shown in Fig 6, the hot face of the test sample may be held within ±2°F. over an extended period. The greatest sensitivity is obtained when the control couple is located as close as possible to the Globars.

The silicon carbide plate, which is located between the Globars and the test sample, levels out temperature fluctuations and maintains more uniform temperature distribution over the hot face of the test sample.

(2) Water System

The water system operates as a closed recirculating system as shown in Fig. 7. Water flows down from the upper constant-head tank through the calorimeter system and into the lower tank, from which it is returned to the upper tank by a centrifugal pump. A thermostat, *F*, inserted in the feed line to the calorimeter system, controls the amount of cooling water which flows through coil *A* by operating the magnetic valve, *E*. The temperature of the water entering the calorimeter may thus be held constant within ±0.5°F. The temperature-control point of the thermostat is set to operate at room temperature to reduce the possibility of heat transfer between the room and the calorimeter system.

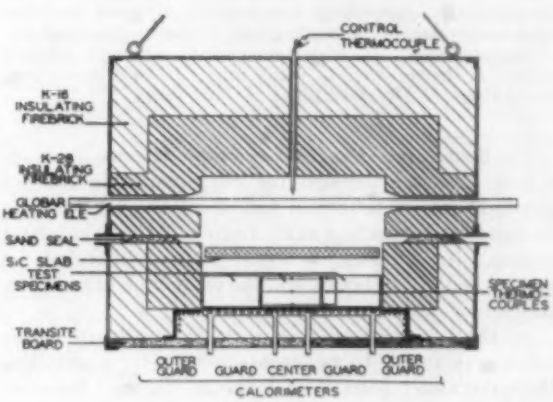


FIG. 5.—Diagrammatic section through furnace.

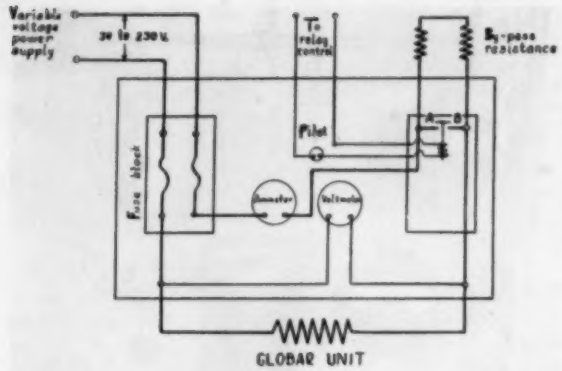


FIG. 6.—Circuit between power supply and heating unit.

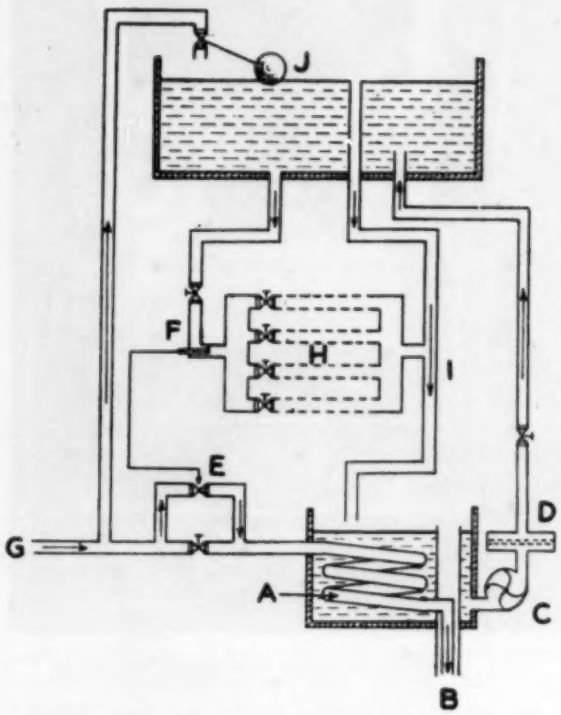


FIG. 7.—Water-circulating system with provision for automatically controlling temperature of water entering calorimeter system; *A*, cooling coil; *B*, connection to drain; *C*, water pump; *D*, water filters; *E*, magnetic control valve; *F*, thermostat; *G*, water inlet; *H*, calorimeter and guard rings; *I*, overflow pipe; *J*, float valve.

The float valve, *J*, is used as a safety device to insure a flow of water through the calorimeters in case of power failure, mechanical failure of the pump, or a broken hose connection at the bottom of the calorimeter system. This tester is usually left unattended for periods of 12 to 16 hours, and the protection afforded by this safety device is necessary.

At the beginning of this work, the ordinary needle valve was found to be unsatisfactory for controlling the calorimeter flows. With special valves,* however,

* Valves made by Hauck Manufacturing Company.

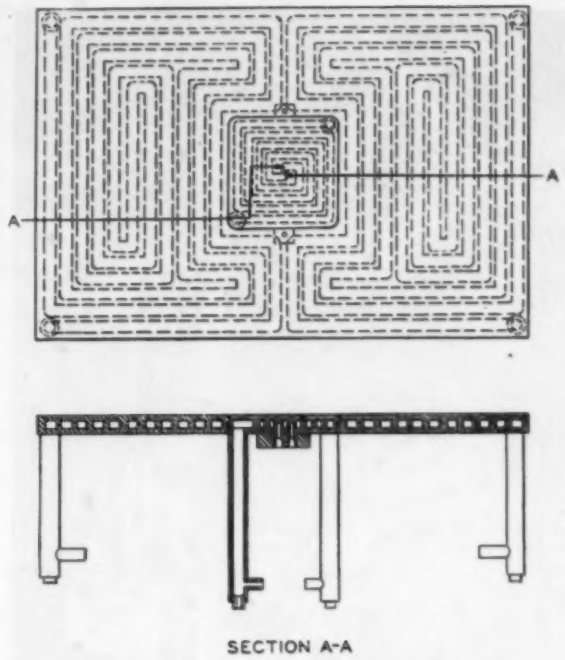


FIG. 8.—Calorimeter and guard ring construction.

and with filters placed in the entering water line, the flow may be held constant to ±0.5% over long periods.

(3) Calorimeter System

The copper calorimeter and guard plate are somewhat different from the designs used by Wilkes,[2] Austin,[3] or Sullivan.† Figure 8 shows the arrangement of the water passages. The main feature of this construction is to have adjacent hot and cold channels to maintain uniform temperature distribution over the entire surface. The guard plate has two inlets and two outlets, whereas the calorimeter has one inlet and one outlet. An outer guard is also used, which extends down to the base of the tester to act as a screen to prevent heat from flowing around and under the calorimeter (see Fig. 5).

Several methods of holding the inner calorimeter were tried. At first, a spring suspension was used, which was designed to allow the calorimeter to exert a constant force even if some bowing of the sample should occur. This method, however, was abandoned, because of difficulties in maintaining uniform pressures. Figure 9 shows the variations resulting from moderate and high-spring tensions on the suspension.

A better method was developed in which the center calorimeter is held rigidly at the same level as the guard plate. In another method, the opening between the calorimeter and guard plate was filled with asbestos paper and wedged in place at several points. In the method finally adopted, the gap between the two was filled with heat-setting cement,‡ which was then cured while the units were clamped firmly together.

† J. D. Sullivan, private communication.

‡ Central Scientific Co., Bakelite cement, No. 11420-B.

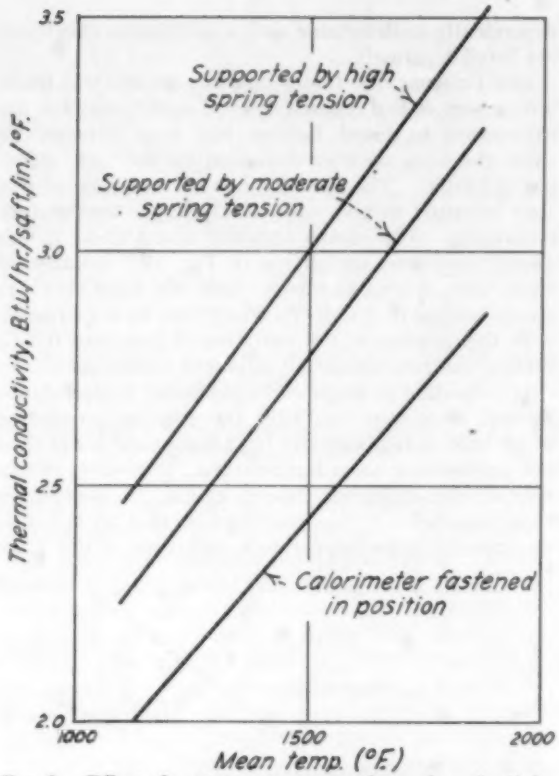


FIG. 9.—Effect of contact pressure on thermal conductivity with calorimeter supported by springs.

Test runs were made to determine the effect of using a different calorimeter level from that of the guard plate and also the effect of pressure when the same levels were maintained. A variation of 10% occurred when the calorimeter was 0.02 in. out of level, whereas the effect of pressure on a level assembly was negligible.

Because the exact alignment of the calorimeter surface is important, the Bakelite cement joint was considered to be the most durable even though this construction proved to be slightly less sensitive on calorimeter-to-guard balancing.

All thermometers were eliminated from the calorimeter system. Multiple differential couples were used to measure the temperature rise of the water as well as the balance between the calorimeter and guard plate. Readings could thus be taken at the entrance and exit ports of the calorimeter plates, and the possibility of error introduced by reading temperatures at thermometer wells located several feet away from the actual calorimeter was also eliminated.

(4) Thermocouple System

The temperature rise of the water flowing through the center calorimeter was measured by a 10× differential copper-constantan thermocouple, which gives an electromotive force of 1 mv. per 2.45°C. Sufficient precision may be obtained by using this thermocouple and a semiprecision type of potentiometer,* and the more sensitive type K instrument is not required.

Figure 10 shows the details of construction of the differential couples for measuring the temperature rise of water in the calorimeter.

The balance between the center calorimeter and guard plate was measured by a 10× copper-constantan differential couple located in four wells in the bottom surface of the copper plates. Five junctions were located in each well; two of these in the inner calorimeter and two in the guard plate.

The balance between the exit flows from the two sides of the guard plate was measured by a 5× differential copper-constantan couple located at the exit ports of the guard plate.

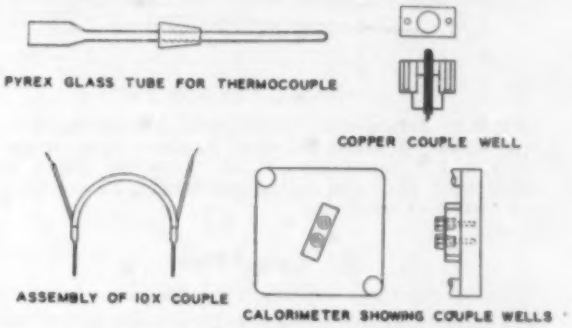


FIG. 10.—Calorimeter and multiple couple assemblies.

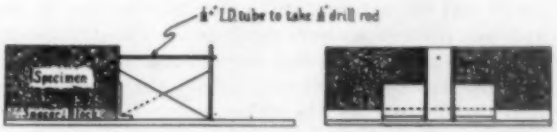


FIG. 11.—Jig for drilling specimens for thermocouple.

Thermocouples were also used to measure the temperature drop through the test sample. These were No. 28 bare wire couples, Chromel-Alumel for temperatures up to 1400°F. and platinum-platinum 10% rhodium above 1400°F. Three couples were used for insulating firebrick, one at the center and two others close to the hot and cold faces, respectively. Surface couples were eliminated by drilling through the brick approximately 0.2 in. from the upper and lower surfaces and threading the couples into the holes without using cements or other filling compounds. The center couple was also located in a similar drilled hole. This method saves considerable time, eliminates surface effects, and does not require stapling or cementing. Figure 11 shows a convenient drilling jig for boring these holes accurately. A piece of $^1/_{32}$-in. drill rod was used, which was rotated by a small portable electric grinding tool. This drill produces a hole slightly smaller than the couple bead so that it is held firmly in position.

An equivalent technique has not been worked out for dense refractories, and surface couples are still used.

* Leeds & Northrup semiprecision-type potentiometer, No. 8862.

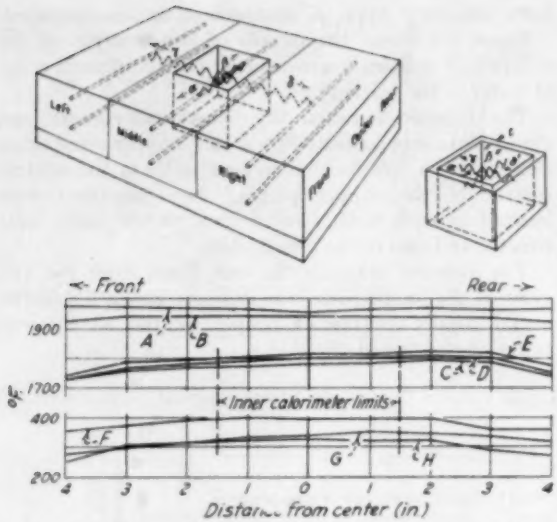


FIG. 12.—Arrangement for determining losses caused by lateral flow; *A*, above SiC slab; *B*, above brick surface; *C*, *D*, and *E*, top couples, 0.2 in. below top surface of specimens; *F*, *G*, and *H*, bottom couples, 2.3 in. below top surface of specimens.

III. Lateral Flow

One of the most important conditions to be maintained in any form of tester is a straight-line flow of heat from the hot to the cold surface. Figure 12 shows the arrangement whereby the amount of lateral flow was calculated. A temperature survey at two levels was made, and the temperature gradients along the 13.5-in. and 9-in. dimensions were computed. The calculations for lateral and vertical flow show that only 3.2% of the heat received by the hot face is dissipated laterally and that 96.8% reaches the calorimeter. This figure of 3.2% is actually high, inasmuch as the gradient is much flatter over the calorimeter area than the average gradient used and the heat loss resulting from lateral flow, therefore, is more nearly 2%.

The temperature gradient (Fig. 12) from the center of the test brick, measured laterally, in the α, β, γ, and δ directions was, respectively, 11°, 7°, 10°, and 3°F. per 1.5 in. at the upper level. The corresponding temperature gradient was 5°, 2°, 23°, and 20°F. at the lower level. An average of these figures gives a lateral temperature gradient of 6.7°F. per in. The lateral flow was computed across a 0.1-in. thick section surrounding an assumed block, 3 by 3 by 2.5 in., in the center of the test brick.

$$\text{Lateral flow } Q_l = \frac{1.1\times(2.5\times12)\times0.67}{144\times0.1} = 1.54 \text{ B.t.u./hr.}$$

$$\text{Vertical flow } Q_v = \frac{1.1\times9\times1440}{144\times2.1} = 47.1 \text{ B.t.u./hr.}$$

$$\text{Lateral flow} = \frac{Q_l\times100}{Q_l+Q_v} = 3.2\%.$$

IV. Effect of Variables on Measured Heat Flow

Several other factors affect the precision of heat-flow measurements. These variables were investigated independently to determine their quantitative effect and are listed separately.

(*A*) *Calorimeter to Guard Balance:* A test was made after a sample had reached thermal equilibrium and the calorimeter to guard balance had been adjusted to show the least possible deflection on the 10× differential couple. The flow through the calorimeter was then adjusted to give successively larger temperature differences. The results obtained under these unbalanced conditions are shown in Fig. 13. Because of these tests, it was decided to hold the calorimeter to guard balance to ±0.07°F., which may be done readily with this apparatus. A variation of less than 0.05% is obtained from completely balanced conditions.

(*B*) *Relation of Room and Calorimeter Temperatures:* Several tests were run with the entering circulating water held at temperatures both higher and lower than the surrounding room temperature. The effect of this temperature difference, shown in Fig. 14, was larger than expected. It was therefore decided to maintain an entering water temperature difference of not more

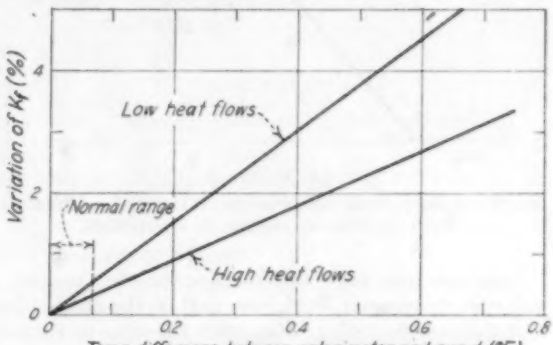


FIG. 13.—Effect on conductivity of temperature difference between calorimeter and guard.

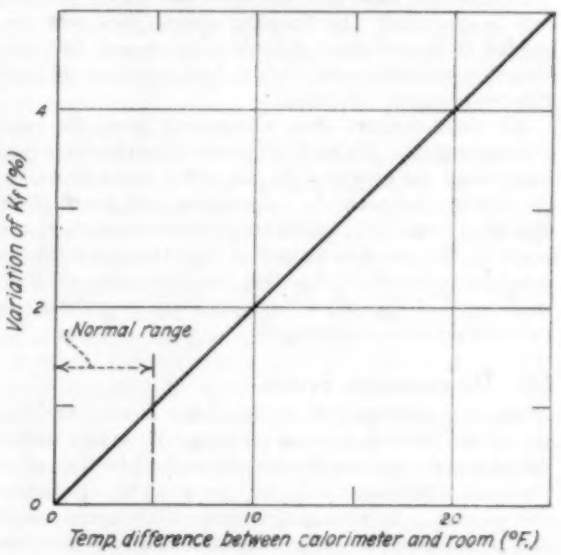


FIG. 14.—Effect on conductivity of temperature difference between calorimeter and room temperature.

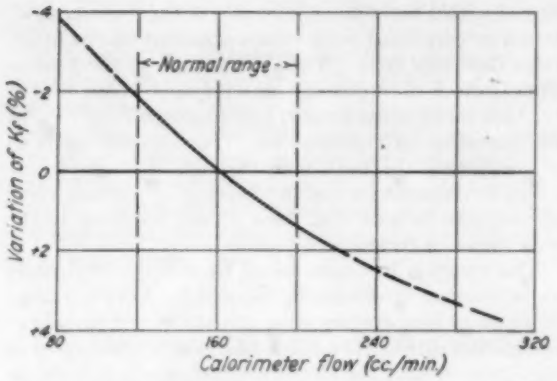


FIG. 15.—Effect on conductivity of variations in water flow through calorimeter.

than ±5°F. from that of the surrounding room temperature, which would cause less than 1% of variation.

(*C*) *Effect of Temperature Rise in Calorimeter:* A considerable range of water flow through the calorimeter is obviously possible for a given condition of heat flow. A high rate of water flow through the calorimeter causes a relatively low rise in temperature, and a low rate of flow causes a greater temperature rise. A series of tests was run under balanced conditions using different rates of water flow. A slight difference in the computed values of k_f occurred when the rate of flow was varied. Figure 15 shows that this difference amounts to about 4% when the flow is doubled in certain ranges. No clear explanation of this effect can be given at this time. By maintaining the calorimeter flow within the "normal range" (Fig. 15), the total variation from the upper to lower limit is less than 2%.

(*D*) *Sample Thickness Precision:* Using the method described here for installing the thermocouples, the insulating firebrick sample may be cut at a point close to the couple locations, and by grinding down carefully, the couple beads may be exposed in place. The distances measured represent the actual separations during the run if the slight thermal expansion of the sample is neglected. The precision of the cold measurement is about ±1%, whereas the change in position caused by thermal expansion is less than 1.0%.

(*E*) *Precision of Measuring Calorimeter-Temperature Rise:* The 10× differential couple, which measures the temperature rise in the calorimeter, was calibrated with precision thermometers in water baths, carefully stirred, at the range in which it was to be used. One couple in use for nearly twelve months has shown no noticeable shift in calibration during this period. For an average calorimeter temperature rise, the measured electromotive force is approximately 1 mv., so that the sensitivity of this reading is approximately 1% with the type of potentiometer used.*

(*F*) *Stray Electromotive Force from Power Line:* At the beginning of this work, some trouble was encountered, which was caused by the effect of the induced electromotive force on the readings of the sample thermocouples. This was noticeable when the furnace was operated at high temperatures with the Globars in contact with the hot brickwork. Grounding the thermocouple circuit aggravated the condition, but the effect became negligible by using an ungrounded circuit and resting the bars on bushings at a cooler portion of the wall.

V. Conductivity Determination on Insulating and Dense Firebrick Samples

The conductivity curves of six brands of commercial insulating firebrick are shown in Fig. 16. Brands A, B, and D, which were run on the low-temperature plate tester, show excellent agreement at the low ends of the curves. At low mean temperatures, the conductivities are proportional to the bulk densities in all cases, but this relation does not occur at higher temperatures

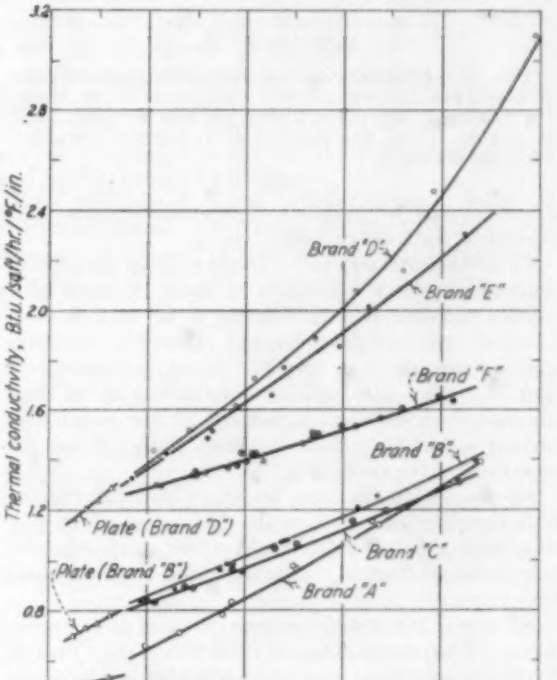
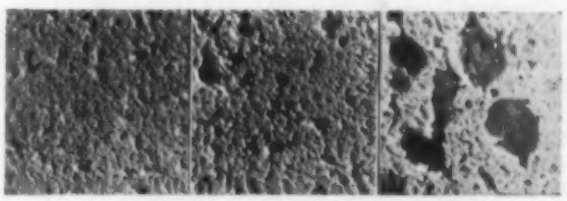


FIG. 16.—Thermal conductivity values determined on apparatus showing plate-tester points for comparison; brand densities (lb. per cu. ft.): *A*, 19.7; *B*, 27.6; *C*, 30.8; *D*, 39.9; *E*, 39.8; and *F*, 37.8.



Fine Intermediate Coarse

FIG. 17.—Pore structure of three insulating firebrick having same bulk density and made from same ingredients.

* See star footnote, p. 455.

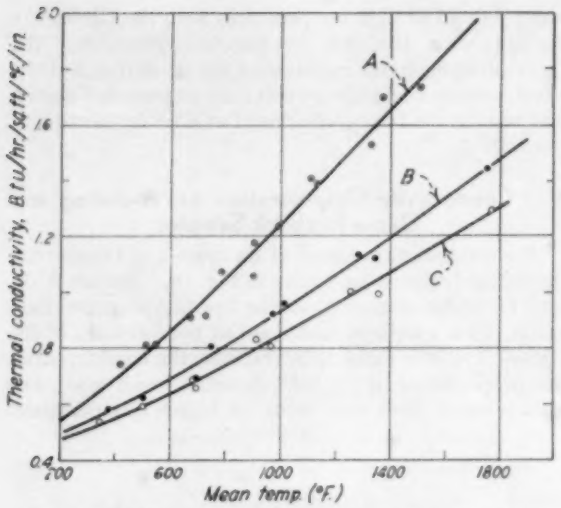


FIG. 18.—Effect of pore size on thermal conductivity; *A*, coarse pores, 1.04 lb. per 9-in. straight, 17.76 per lb. cu. ft.; *B*, intermediate pores, 1.01 lb. per 9-in. straight, 17.27 lb. per cu. ft.; *C*, fine pores, 1.01 lb. per 9-in. straight, 17.27 lb. per cu. ft.

where transfer by radiation constitutes a greater percentage of the total transfer.

To investigate this point further, three samples of insulating firebrick were made up, using the same basic composition and maintaining the same bulk density. The pore structure, however, was different in the three samples, ranging from very fine to very coarse texture (see Fig. 17). Conductivity determinations on these samples show excellent agreement at low mean temperatures, but they differ by more than 50% at the upper end of the curve (Fig. 18).

By measuring the pore structure and determining bulk density, some empirical relationship might possibly be established which would permit an approximate calculation of thermal conductivity for different refractory materials.

Relatively few tests have been made on dense refractories. The results obtained from preliminary runs on duplicate samples of Star brand silica brick, which were used in the cooperative tests described by Nicholls[1] fell at the lower limit of the band of values reported. Further work is being done to establish a more satisfactory procedure for determinations on dense refractory samples.

VI. Verification and Duplication of Results

Duplicate samples of several brands of insulating firebrick were tested in a guarded hot-plate tester at low mean temperatures. These values showed close agreement with results which have been obtained on the tester described here (see Fig. 16). The Johns-Manville Company also tested three duplicate samples over the entire temperature range in which a modified form of the apparatus described by Weinland[4] was used. The test results agreed within less than 5% for two of the three samples tested as compared with values obtained on the apparatus described here. The third sample showed somewhat greater divergence, a difference of about 8% at the high mean temperatures and approximately 15% at the lowest mean temperatures. Because the methods of measuring the heat flow through the sample are basically different for the two types of apparatus, there is reason to believe that these values are close to the true values of conductivity.

The question has been raised by many investigators as to whether errors are introduced by having a large decrease in temperature drop across the test sample as contrasted with a very small decrease. The curves in Fig. 16 show that the slopes are sufficiently uniform to indicate that conductivity values obtained by using a great decrease in temperature are equivalent to those determined when a small temperature drop is used. Because the Weinland apparatus uses a much smaller decrease in temperature across the test sample than that described here and because the comparative results obtained showed satisfactory agreement, it is also apparent that a variation in the amount of temperature difference maintained between the hot and cold face of the test sample causes a negligible difference in conductivity determinations for a given mean temperature.

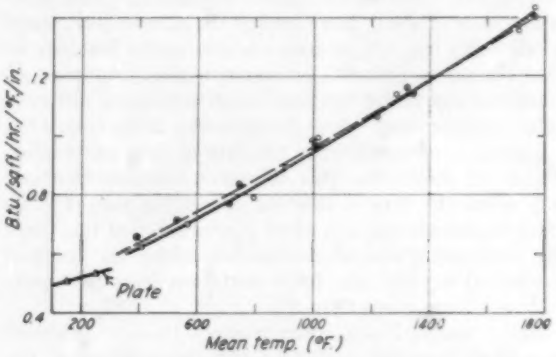


FIG. 19.—Thermal conductivity of duplicate samples determined at different times by different operators.

Figure 19 shows the duplication of results that may be obtained when equivalent samples are tested by different operators. A variation of about 2% occurs over the complete range of the curves.

A second tester built recently duplicates the one described here. With the same operating procedure and by interchanging the same samples from one tester to the other, a variation of only 3 to 4% was obtained. This shows that good reproducibility may be obtained by different laboratories if standardized construction and operation are followed.

VII. Summary

(1) A Globar-heated, water-flow calorimeter is described which gives values for insulating firebrick at low mean temperatures that agree well with values obtained on a guarded hot plate tester.

(2) Test runs, covering a complete temperature

[4] C. E. Weinland, "Method of Measuring Thermal Conductivity at Furnace Temperatures," *Jour. Amer. Ceram. Soc.*, **17** [7] 194–202 (1934).

range, may be made in three to four days with this apparatus.

(3) Satisfactory agreement has been obtained between the Globar tester and a modified form of the tester described by Weinland.

(4) A duplicate tester has been constructed which gives close agreement with the other unit when the same samples are interchanged.

(5) By standardizing construction and operation, good reproducibility may be obtained between different testing laboratories.

Acknowledgment

The writer wishes to acknowledge the careful and painstaking work of V. J. Duplin, Jr., and T. W. Ratcliffe in the construction and operation of this apparatus; T. C Patton has also made valuable contributions. In addition, the advice of F. H. Norton, in the preliminary part of this work, data supplied by G. B. Wilkes, and the assistance of H. W. Culp in the preparation of the illustrations have been of great value. The writer also acknowledges the fine cooperation of G. A. Downsbrough and C. B. Bradley of the Johns-Manville Research Laboratory.

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CONTROL TESTING FOR CONSISTENCY OF REFRACTORY MORTARS*

By Earl C. Petrie and D. W. Kocher

Abstract

Various methods of determining the consistency of mortars are discussed, and data are included to show the test results obtained on different instruments. A description is given of a modified Vicat needle which may be used for the control of consistency during the manufacture of wet-type, cold-setting mortars.

I. Introduction

For several years there has been a need for some type of equipment which would definitely express numerical values for the consistency of wet-type, cold-setting refractory mortars.

Consistency is used in a descriptive or qualitative sense only in this paper. The terms "workability" and "consistency" refer to complex qualities not capable of direct measurements. The term "workability" represents a quality that cannot be measured in the fundamental units of mass, length, and time. The term "consistency" can be, and has been, applied to every thing from gases to crystalline solids. Despite the complex nature of the meaning of these words, they undoubtedly reflect a sensory perception of certain combined qualities with which everyone is familiar.

Most consumers of refractory mortars depend on the manufacturer to furnish a product having the workability or consistency best suited for their individual needs. Because there has been no satisfactory method of measuring consistency, considerable variation in this property has occurred in spite of strenuous efforts at control. There are several factors which may cause the product to have a higher or lower consistency; for instance, the mixing water may be too high or too low, the sodium silicate content may be allowed to vary, an increase in the moisture content of the inert material and clay may occur, or an adverse reaction may take place between the sodium silicate and the plastic clay vsed. These factors might be controlled if they occurred singly, but because they vary together, they may cause wide differences in the consistency of wet-type, cold-setting mortars. It has seemed that if suitable test equipment were available these variations in the finished product could be practically eliminated. The test equipment should be simple to operate and easily cleaned, and it should yield accurate and quickly evaluated results.

The literature indicates several different types of equipment which might be applicable to tests on the reference mortars. In this study, three types were selected and tested to determine their suitability.

II. Flow Trough

This equipment (Fig. 1) has been used for several years in testing various mortars. Six experimental lots of wet-type, air-setting mortars were tested in the present study. The water content of these mixes varied from 13.28 to 19.61%; this range in moisture content included one mortar stiff enough to form thick trowelled joints and one mortar thin enough for poured or dipped joints. No flow occurred in the first five lots tested, and there was only $^1/_{16}$ in. of flow in the mortar which contained 19.61% of water. A reading of $^1/_{16}$ in., however, is entirely too low for accurate testing purposes. The flow should be in the range of approximately 2 to 3 in. to have reproducible results, and the mortar must contain approximately 22% of water to have a flow in this range.

The policy of most manufacturers of these products has been to furnish to the consumers a more or less stiff mortar, which will permit them to add sufficient water to bring the material to whatever consistency is desired.

As insufficient flow was obtained on the mortar with the highest water content, the flow trough was considered to be unsuitable for testing wet-type mortars with normal water content.

III. Hommel Viscometer

The Hommel viscometer, which is frequently used in the enamel industry to control slip viscosity, has an open-end tube with one end formed into a truncated cone, and it is furnished with two orifices. Exactly

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Refractories Division). Received May 13, 1942.

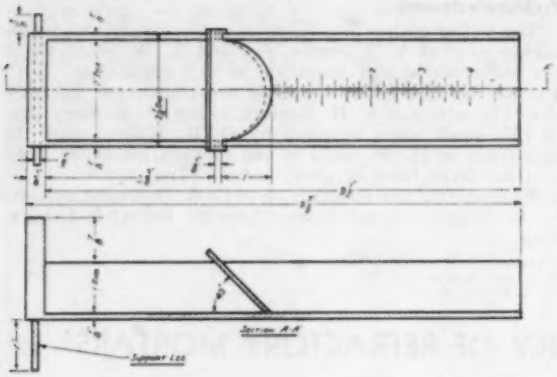

FIG. 1.—Equipment used to test various mortars.

200 cc. of the test material is introduced into the tube, and the time required for a portion to flow through either orifice is measured. No flow was found to occur with the larger orifice even with the mortar which contained the highest water content. If this equipment were used to evaluate the consistency of wet-type mortars, a water content of at least 22% would be necessary to obtain satisfactory readings. As no test data could be obtained using mortars with normal water content, the Hommel viscometer was considered to be unsuitable for testing wet-type refractory mortars.

IV. Modified Vicat Apparatus

The Vicat needle has found wide use in the determination of the plasticity of clays in the pottery industry and in testing the consistency of many other materials. Modified types of this equipment have been adopted by the A.S.T.M. to determine the consistency of neat Portland cement, calcined gypsum, and gypsum mixtures.

The equipment used for testing gypsum and gypsum products (Fig. 2) consists of a bracket, *A*, bearing a movable brass rod, *B*, 6.3 mm. in diameter and of suitable length to fit the Vicat bracket. On the lower end of the rod is a plunger, *C*, 19.0 mm. in diameter and 44.4 mm. in length, made of aluminum tubing. The total weight of the rod with plunger is 50 gm. which may be increased by means of a weight, *D*, screwed into the rod. The rod may be held in any vertical position by means of a screw, *E*, and it has a mark midway between the ends which moves under a scale, *F*, graduated in millimeters, attached to the bracket, *A*.

In the work on the wet-type, air-setting refractory mortars, two instruments were used. One was identical to that used in testing gypsum mixtures except for the weight of the rod, and the other was somewhat larger and had a much longer scale so that it could be used to test mortars of long-range consistency (Fig. 3). The latter equipment was provided with two plungers, one with a flat end and the other with a hemispherical end. The flat-end plunger was 127 mm. long and 25.4 mm. in diameter. Stainless steel tubing was used to insure a smooth surface and to prevent rusting and pitting. The hemispherical end plunger was 138.2 mm. long and 25.4 mm. in diameter and was also made from stainless steel tubing.

The total weight of the flat-end plunger assembly was 326 gm., and the weight of the hemispherical end-plunger unit was 338.6 gm.

In obtaining the data on the modified Vicat apparatus, the mortar was thoroughly mixed by hand in its original container. A definite quantity was transferred to the metal cups to give an initial reading of 1 to 5 when the needle just touched the mortar. The mortar was then stirred vigorously with a spatula in a manner to avoid forming air bubbles. After this stirring, the cup was bumped on the bench three or four times to give a smooth surface to the mortar. (This bumping also indicates the presence of air bubbles; if air bubbles are present, they will rise to the surface, causing a slight bulge, and the sample should be discarded.)

The cup was placed under the plunger or needle, which was lowered in the center of the cup until it

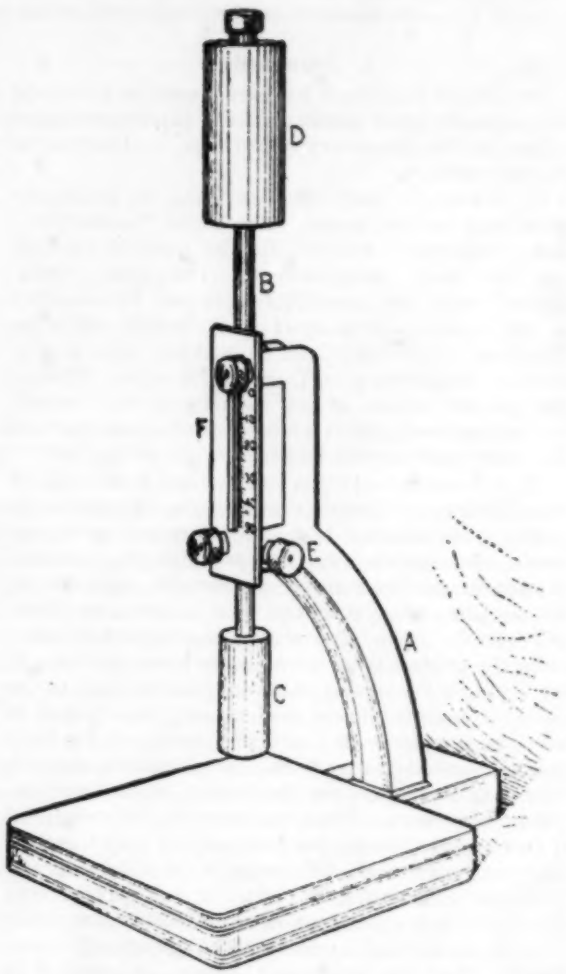

FIG. 2.—Modified needle Vicat apparatus for tests on gypsum; *A*, bracket for removable brass rod, *B*; *C*, plunger; *D*, weight screwed into rod; *E*, screw; *F* scale in graduated millimeters.

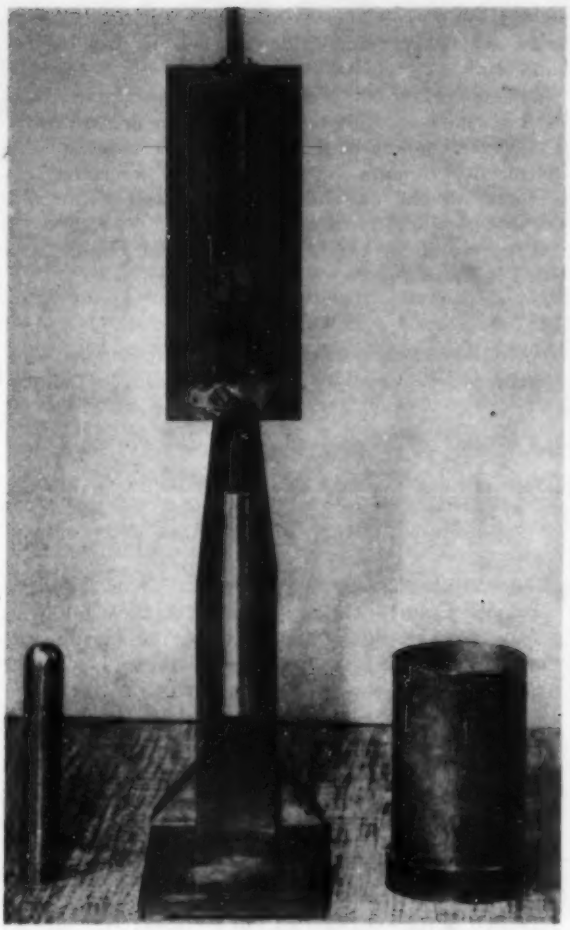

FIG. 3.—Instrument used to test mortars of long-range consistency.

just touched the surface of the mortar, and the setscrew was then released, allowing the plunger to settle into the mortar. It was permitted to fall free for 30 seconds, which were timed by a stop watch. The final reading was taken, and the total depth of immersion was determined. The mortar was completely removed from the cup, placed back in the original container, and remixed. This procedure was repeated for each test, and three determinations were found to be sufficient to establish a reliable test result.

With the larger apparatus, a similar procedure was followed. The mortar was transferred from the original container and was placed in the special cup or vessel. The sample was thoroughly mixed to eliminate any air bubbles or pockets, and the top was levelled off. The plunger was then lowered in the center of the container until contact was made with the surface of the mortar. The original reading was taken, and the plunger unit was allowed to fall until it came to complete rest. The time required did not exceed 10 seconds. The final reading was taken and recorded. The mortar was returned to the original container and remixed. A total of six readings was taken for each mortar tested.

Inasmuch as the modified Vicat apparatus, which is specified in A.S.T.M. Standard Methods of Test C26 and C77, showed promise, tests were conducted to determine whether it was suitable for manufacturing control of consistency as well as a guide in laboratory testing.

Two experimental mixes with different water contents were made up. Mortar A contained 12% and mortar B contained 15.3% of water. The Vicat consistencies were determined following the usual procedure of using 52.3 gm. for total weight of rod and plunger. Both sample A (12% of H_2O) and sample B (15.3% of H_2O) had values of 15 mm., and the temperature of both samples was 54°F. at the time of testing. From these data, it may be seen that with a change in the water content there is a corresponding change in the penetration, the temperature of both mortars being the same.

During this investigation and also in the laboratory control work, it was noted that the consistency of the test mortars appeared to be affected by temperature change. These changes were not sufficient to reject the mortar from a workability angle, but they could be detected by an experienced operator.

To show the effect of two different temperatures on the consistency of the same mortar, sample B, which contained 15.3% of water, was tested at 55°F. and at 73°F. ± 1°. Table I shows the results obtained on this sample, as well as the effect of varying the weight of the plunger rod assembly and the temperature when the size of the plunger or needle remained the same.

TABLE I

VICAT CONSISTENCIES (SAMPLE B)

Rod total wt. (gm.)	At 55°F. (mm.)	At 73°F. ± 1° (mm.)
41.6	12	5
52.3	15	7
62.3	19	8
72.3	22	10
102.3	33	18

To study the sensitivity of the instrument, 1% of water was added to sample B, the weight was increased in definite increments, and the size of the needle was kept constant. As a further check on the effect of temperature variation, this sample with an increased water content was also tested at two temperatures (see Table II).

TABLE II

VICAT CONSISTENCIES (SAMPLE B)

Rod total wt. (gm.)	At 56°F. (mm.)	At 73°F. (mm.)
41.6	15	7
52.3	22	10
62.3	24	11
72.3	26	15
102.3	39	23

In order to show the adaptability of the modified Vicat apparatus, increasing amounts of water were added to sample A. The consistencies were determined at two different temperatures with the plunger

size and weight of the assembly kept constant (see Table III).

TABLE III

ADAPTABILITY OF MODIFIED VICAT APPARATUS

Water added (%)	Vicat consistencies	
	At 56°F. ± 1°	At 73°F. ± 1°
0	5	3
1	8	5
2	14	7
3	21	11
4	31	18
5	38	25
6	No results	30
7		38
8		No results

The results shown in Table III indicate that with slight increases in the water content a corresponding increase is noted in the Vicat consistency, the increases occurring at both testing temperatures.

In the present work with the modified Vicat apparatus, considerable care in testing procedure must be observed or gross errors will result from the following causes: (1) wide variations in temperatures of the same test sample; (2) failure to keep the rod clean and oiled; (3) failure to clean and dry the plunger after each determination; (4) failure to give each sample the same amount of stirring or mixing; (5) failure to have the mortar free from lumps and air bubbles (these may be detected by an experienced operator by watching the fall of the plunger, which should come to a smooth stop); (6) turning the setscrew too tightly when holding the rod, which causes a drag on the rod when it is released; a trigger arrangement for releasing the rod should be provided; (7) vibration of the bench or table during the falling period; (8) failure to keep the rod in a vertical position; and (9) varying the time between the stirring in the cup and the release of the rod; this is especially important in mortars which gel quickly, such as the dry, cold-setting mortars.

In collecting the data for this paper and in laboratory control work, it has been found that operators of different experience can check within ±2 mm. and 90% of the time within ±1 mm.

The greater portion of the data was obtained on the modified Vicat apparatus. In the work with this instrument, it was noted that some improvements might be made in the construction, especially in the length, weight, and size of the plunger or needle. As the depth of penetration on the modified apparatus cannot exceed 44 mm., it was believed desirable to have an instrument which could be used to determine the penetration on rather thin samples. To accomplish this, it was necessary to redesign the modified Vicat apparatus. The general design of the modified instrument was followed except that provisions were made to allow for a penetration of at least 100 mm. This larger equipment is somewhat more flexible than the modified type because thinner mortars may be tested and also because deeper penetrations may be obtained on thicker mortars by adjusting the weights on the top of the plunger rod. It is thought that more more accurate results may be obtained if the penetrations are deeper on thicker mortars as well as on thinner types.

In the work in which the redesigned equipment was used, the mortars were tested at only one temperature. The water content was varied, and the weights were increased in definite increments. This procedure was followed for the flat end plunger as well as for the hemispherical end type.

The results on the hemispherical end plunger are listed in Table IV.

TABLE IV

VICAT CONSISTENCIES WITH HEMISPHERICAL END PLUNGER

Water added (%)	Normal wt. (mm.)	100 gm. added (mm.)	200 gm. added (mm.)
0	9	11	14
1	12	18	25
2	29	40	44
3	40	55	64
4	58	72	84
5	81	100	No result

The Vicat consistencies shown in Table IV were obtained in exactly the same manner as those obtained on the modified apparatus, that is, the mortar was thoroughly mixed in the original container before the required amount was placed in the cup or receptacle. The plunger was then lowered until it just came in contact with the top of the mortar, the original reading was taken, the plunger allowed to fall free until it came to complete rest (approximately 10 seconds), and the final reading was taken and recorded. After each reading, the mortar must be returned to the container and thoroughly remixed, otherwise lower penetrations results will be obtained.

Similar tests were carried out by using the flat end plunger and by varying the water content and total weight on the plunger rod assembly. The results are shown in Table V.

TABLE V

VICAT CONSISTENCIES WITH FLAT END PLUNGER

Water added (%)	Normal wt. (mm.)	100 gm. added (mm.)	200 gm. added (mm.)
0	4	6	8
1	5	10	15
2	13	20	26
3	22	35	42
4	41	60	73
5	62	81	94

The Vicat consistencies shown in Table V were also obtained following the usual procedure of mixing the mortar carefully before allowing the plunger to fall. The plunger or needle was carefully cleaned and dried before each determination.

V. Summary

In summarizing the results on both instruments presented here, the writers believe that either instrument would be satisfactory for plant or laboratory control of the consistency of wet-type, air-setting refractory mortars. The larger equipment is some-

what more flexible in operation because of the longer plungers which permit tests on rather thin cements. A greater depth of penetration can also be obtained when thick mortars are tested by adjusting the weight of the plunger rod assembly. The smaller unit, however, is somewhat lighter in weight and easier to handle.

The general advantages of both instruments may be listed as follows: (1) They are easy to operate; (2) accurate results may be obtained; (3) they are easily cleaned; (4) they may be used to determine gelling or setting up in containers on long or short periods of storage; this use differs from other tests because the mortar must be removed from the container before testing; (5) penetration results may be obtained quickly; and (6) the results may be quickly evaluated.

The modified Vicat apparatus has been adopted by this laboratory for all tests on the reference mortars. The practice is to bring the mortars to a certain consistency before any tests are started. The results, therefore, do not depend on the judgment of any one individual as to whether two or more mortars have the same consistency. The writers have found that this procedure has worked very well on all of the various tests, such as those relating to water retention and to forming the joints for the modulus of rupture test.

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RESISTANCE OF ENAMELS TO THERMAL SHOCK*

By E. E. Howe and E. P. Bolin

Abstract

Thermal-shock resistance tests were made on enamels of varying thermal expansions applied on test pans. Increased weight of application and high expansion of the cover coat decreased the thermal-shock resistance, whereas high expansion of the ground coat increased the resistance.

I. Introduction

Kitchenware in service is subjected to thermal changes, and numerous investigations have been conducted to establish factors that contribute toward good thermal-shock resistance. A review of the literature reveals that one of the earliest papers published in this country relating to this problem was written by Sweely,[1] who reported that a light total ground-coat and cover-coat enamel application in conjunction with a high-expansion ground coat gave the best resistance to thermal shock.

A more complete study by Danielson and Sweely[2] confirmed the earlier data and showed further that a low-expansion cover coat, in combination with a ground coat having an equal or greater expansion than the cover coat, gave the best thermal-shock resistance. Conducting a similar study, McIntyre[3] verified the findings of Danielson and Sweely and, in addition, found that a lighter gauge of metal reduced the resistance to thermal shock.

In contrast, Sasse[4] reported that ground-coat expansion should be low rather than high. In his study, however, the listed thermal-expansion values of the ground coat were relatively high.

Stuckert[5] reported that thermal resistance is best when expansion is low and elasticity high, but another author[6] indicated that the silica should be kept as high as possible in the enamel formulation. Vielhaber[7] mentions that bubble structure of the fired enamel affects this property of the enamel.

Various methods and apparatus for testing thermal-shock resistance of enamels have been described by Landrum,[8] Kinzie,[9] and Shands.[10]

II. Experimental Procedure

(1) Preparation of Samples

The frit combinations employed in this study included two ground coats and four cover coats having varying amounts of expansion. A ground-coat combination of two frits, with a mean expansion as shown in Table I, was selected as a standard for comparison; another ground coat had a higher expansion; and a

* Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April 22, 1942 (Enamel Division). Received April 22, 1942.

[1] B. T. Sweely, "Relation of Composition of Thermal Shock in Steel Enamels," *Jour. Amer. Ceram. Soc.*, **5** [5] 263–65 (1922).

[2] R. R. Danielson and B. T. Sweely, "Relation Between Composition and Properties of Enamels for Sheet Steel," *ibid.*, **6** [10] 1011–29 (1923).

[3] G. H. McIntyre, "Physical Testing of Porcelain Enameled Hollow Ware," *Proc. Porcelain Enamel Inst. Forum, First Forum, May, 1937*, pp. 155–63; *Ceram. Abs.*, **18** [1] 12 (1939).

[4] Heinrich Sasse, "Cracked Cooking Utensils," *Emailwaren Ind.*, **11** [6] 47–50 (1934); *Ceram. Abs.*, **13** [7] 171 (1934).

[5] L. Stuckert, "Expansion of Enamels," *Ceram. Age*, **17** [5] 269–72 (1931); *Ceram. Abs.*, **10** [11] 756 (1931).

[6] "Thermal and Chemical Resistance of Enamel for Sheets," *Glashütte*, **58**, 816–18 (1928).

[7] L. Vielhaber, "Determining Physical Properties of Enamels," *Emailwaren Ind.*, **16** [31–32] 205–206 (1939); *Ceram. Abs.*, **19** [1] 6 (1940).

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[9] C. J. Kinzie, "Physical Tests for Vitreous Enamels," *Jour. Amer. Ceram. Soc.*, **12** [3] 188–92 (1929).

[10] E. H. Shands, "Thermal-Shock Test for Porcelain Enamel, I–II," *Amer. Enameler*, **5** [2] 8–9; [3] 11 (1932); *Ceram. Abs.*, **11** [11] 555 (1932).

TABLE I

THERMAL EXPANSION MEASUREMENTS

Enamel combinations* (1)	Ground-coat thermal expansion × 10^{-7} 97°–637°F. (2)	Ground-coat 97°F.–softening temp. (3)	Cover-coat thermal expansion × 10^{-7} 97°–637°F. (4)	Cover-coat 97°F.–softening temp. (5)	Avg. thickness (in.) (6)	Thermal shock (7)
GA†	300.0	415.5	290.0	389.0	0.0064	6.5 ± 2.2
GA	"	"	"	"	.0100	3.5 ± 0.81
GA‡	"	"	"	"	.0159	1.0 ± 0
GA 1	"	"	"	"	.0113	2.6 ± 1.3
G 1 *A*	"	"	"	"	.0117	3.0 ± 1.8
GB	"	"	333.0	429.0	.0103	1.0 ± 0
GC	"	"	280.0	396.3	.0110	4.2 ± 2.6
GD	"	"	265.0	392.0	.0109	9.9 ± 0.22
HGA	310.0	441.0	290.0	389.0	.0086	6.7 ± 1.3
HGD	"	"	265.0	392.0	.0102	+12.0 ± 0

* Enamel description: *G*, standard ground coat; *A*, standard cover coat; *B*, high-expansion cover coat; *C*, medium low-expansion cover coat; *D*, low-expansion cover coat; *G* 1, standard ground-coat, low-bubble structure; *A* 1, standard cover-coat, low-bubble structure; and *HG*, high-expansion ground coat.
† One cover-coat application. ‡ Three cover-coat application.

third variation was made by substituting a clear clay for the opaque clay in the mill addition to obtain less bubble structure.

An acid-resistant, cover-coat frit was selected as a standard, and a nonacid-resistant enamel was used to give a high expansion. Medium low- and low-expansion enamels, both acid resistant, were used to secure varying degrees of thermal expansion. As a further variation, the standard cover coat was milled with a clear clay instead of an opaque clay to obtain less bubble structure.

Frit charges of 25 lb. were milled with 7% of clay and suitable electrolytes to obtain proper dipping consistency. Before enameling, 2-quart, 26-gauge pudding pans, formed with a flat bottom, were given a pickling treatment. This treatment included an alkaline cleaning, 7% hot sulfuric acid pickle, nickel flash, and a soda ash-borax neutralization.

The ground coats were set to dip $1^1/_8$ oz. per sq. ft. (dry), and they were manipulated with tongs to secure an even coating. They were supported under the flange and fired at 1560°F. for 3 minutes. The enamel thickness of the inside bottom of each pan was measured by an electric thickness gauge. Only those pans having an enamel thickness of 0.003 to 0.004 in. were utilized for the tests.

The cover coats were set to dip at $1^1/_2$ oz. per sq. ft. (dry), and the enamel was applied to the pans with the aid of tongs. The cover enamels were applied in two coats, except as indicated in Table I, and a total thickness of approximately 0.010 in. was maintained. The same burning tools were used in the firing operation, which was carried on for $2^1/_2$ minutes at temperatures varying from 1500° to 1540°F., depending on the hardness of the enamel involved. A series of ten pans was run on each enamel combination, and the data for thickness and thermal shock shown in Table I are average values.

(2) Thermal-Shock Test

The pans were tested for resistance to thermal shock by placing them in a domestic electric roaster operating at 350°F. The temperature was controlled by a thermostat, which was part of the unit, and the actual temperature was measured with a mercury thermometer inserted through the cover and close to the pan. After allowing the pan to remain $^1/_2$ hr. at this temperature, 50 cc. of ice water were poured into it. The roaster cover was then replaced, and the pan was allowed to remain for an additional $^1/_2$ hr.; at the end of this time, the water had evaporated. If no failure had occurred, the quenching and evaporating cycle was repeated. Failure was considered to have occurred when a small chip of enamel had spalled, although the chip may not necessarily have detached itself from the surrounding enamel. This procedure was carried on for three complete cycles at 350°F., and if there was no evident failure, the temperature was raised 50°F. and the same three-cycle procedure was followed. The test was repeated with the temperature being raised in increments of 50°F. up to and including 500°F., the operating limit of the roaster. In order to evaluate the tests, the pans were rated according to the number of cycles necessary to cause failure. For example, a pan which had received three shocks at 350°F., three at 400°F., three more at 450°F., plus two at 500°F., and failed in the second cycle at 500°F., was given a thermal-shock rating of 11. A pan having a high numerical value would therefore have a high thermal-shock resistance. The average of the values for each set of ten pans was then determined and the standard deviation was computed.[11]

(3) Thermal-Expansion Measurements

The cubical thermal-expansion values shown in Table I were calculated from the linear thermal-expansion curves obtained by the interferometer method using the technique described by Fellows and Howe.[12] The

[11] "A.S.T.M. Report of Committee E-1 on Manual on Presentation of Data, 1933," *Proc. Amer. Testing Mat.*, **33** [Part I] 453–88 (1933); pp. 466–67.

[12] R. L. Fellows and E. E. Howe, "Effect of Mill Additions on Thermal Expansion of Sheet-Iron Ground Coats," *Jour. Amer. Ceram. Soc.*, **19** [4] 109–11 (1936).

"plate" method of preparing the sample for interferometric measurement was used on the ground-coat and nonacid-resistant, cover-coat enamels. The "rod" method was employed on the acid-resistant, cover-coat enamels.

Two cubical thermal-expansion values for each enamel are shown in Table I. The values given in columns (2) and (4) cover the temperature interval from 97° to 637°F., the range below the critical expansion period of enamels and within the limits of temperature encountered in the thermal-shock test. The values given in columns (3) and (5) show the cubical expansion of the enamels from 97°F. to the softening temperature of each enamel.

III. Discussion of Results

(1) Weight of Application

The effect of varying the weight of application of the standard expansion cover-coat enamel on thermal-shock resistance is shown in Fig. 1. The failure cycle in this figure is plotted against total thickness of enamel, and it is evident that the application of additional cover enamel produces a rapid decrease in resistance to thermal shock. The extra cover coat applied to the standard enamel pans reduced the resistance so that every pan failed in the first cycle at 350°F. This series of pans had a thermal-shock value as low as any of those tested, and it equalled those of the high-expansion cover coat which failed in the first cycle at 350°F. Although both enamel combinations, *GA* (three-coat) and *GB*, had the same value for thermal shock, the appearance of the failure was different.

This difference in the type of failure is shown in Figs. 2 and 3. Figure 2 shows the inside bottom of a pan enameled with three coats of a standard-expansion cover coat over the standard-expansion ground coat. The enamel "spalls" in this instance were not released from the surrounding enamel and actually required force with the use of a razor blade to lift and remove the three chips of enamel. In Fig. 3, a high-expansion cover coat over a standard-expansion ground coat, the cover-coat enamel actually spalled off in large chips, exposing the ground coat.

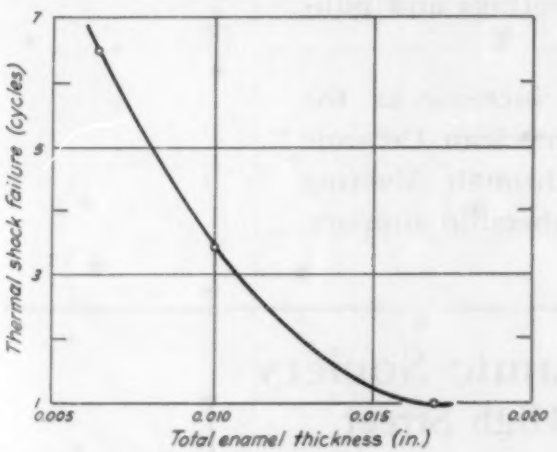

FIG. 1.—Relation between thickness of enamel coating and resistance to thermal shock.

FIG. 2.—Inside bottom of pan showing nature of thermal-shock failure in three-coat standard cover enamel (A).

FIG. 3.—Inside bottom of pan showing type of thermal-shock failure in high-expansion cover enamel (B).

(2) Bubble Structure

It was assumed that the substitution of a clear clay for the opaque clay in the mill addition provides a decrease in the bubble structure in the fired enamel coating, a phenomenon which has been reported by several authors. If a difference in bubble structure was produced by this method, it had no significant effect on the thermal-shock resistance of the enamel. This may be seen by comparing the results shown in Table I for enamels *G1A* (3.0), *GA*1 (2.6), and the standard *GA* (3.5).

(3) Cover-Coat Expansion

A comparison of the results, obtained when the cover-coat expansion was varied keeping the ground-coat expansion constant, may be seen (Table I) by noting the thermal-shock values for enamels *GB*, *GA*, *GC*, and *GD*. Considering the temperature expansion range of 97° to 637°F. these cover coats vary in value from a high of 333.0 (*GB*) to a low of 265.0 (*GD*),

and the corresponding thermal-shock values vary from 1 to 9.9. Although this relationship is not directly proportional, the comparison substantiates the theory that a decrease in expansion of the cover coat increases the resistance to thermal shock. If the values for expansion in the range from 97°F. to softening temperature are used as a basis for indicating thermal-shock value, there is not such a wide variation in expansion, and the results therefore would not be as accurate as in the lower temperature range.

(4) Ground-Coat Expansion

The data also indicate that the use of a higher expansion ground coat, *HGA*, under two coats of the standard-expansion cover coat improved the thermal-shock resistance from 3.5 to 6.7. The cubical expansion difference of the two ground coats varied 10 units when the temperature interval of 97° to 637°F. was considered, whereas in the range of 97°F. to softening temperature, the variation was 26 units.

(5) Ground- and Cover-Coat Expansion Combined

Inasmuch as a high-expansion ground coat and a low-expansion cover coat apparently improved thermal-shock resistance, these two types of enamels were used on one set of pans, *HGD*. The highest thermal-shock value encountered is given in Table I as 12.0 ± 0 because none failed after the third cycle at 500°F.

IV. Conclusions

On the basis of tests conducted on enamels covered by this investigation, it was determined that (1) increased weights of application of cover coats decrease thermal-shock resistance; (2) a decrease in the number of bubbles either in the ground or cover coat, produced by substituting clear clay for opaque clay in the mill addition, has no appreciable effect on the thermal-shock resistance; (3) lowering the thermal expansion of the cover coat increases the thermal-shock resistance; (4) increasing the thermal expansion of the ground coat increases the thermal-shock resistance; (5) the cubical expansion within the range of 97° to 637°F. may be used to evaluate the thermal-shock resistance of an enamel; and (6) a high-expansion ground coat in combination with a low-expansion cover coat produces the best thermal-shock resistance.

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